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THE CHRISTIANSEN EXPERIMENT WITH SPHERICAL PARTICLES

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1. Introduction

During a visit by the senior author to the works of Messrs. Chance Brothers at Birmingham in May 1948, he noticed in their showroom an exhibit of glass in the form of tiny spherules about a millimetre in diameter. A sample of the material very kindly presented by the firm was brought back to India, and the studies now reported were made with it.

On placing a quantity of the substance in a transparent cell and holding it up against a bright source, it is found that even a moderate thickness of it suffices completely to cut off the light and make the cell opaque. When, however, the empty spaces between the spherules of glass are filled by a mixture of carbon disulphide and acetone of suitably adjusted refractive index, the Christiansen effect is observed. In other words, the cell becomes transparent to a restricted region of the spectrum, while the rest of the light appears as a coloured halo surrounding the source when viewed through the cell. The explanation of these facts is obviously the same as in the usual form of the Christiansen experiment. Nevertheless, the phenomena observed are distinctly more spectacular with the spherules than with a pack of irregular fragments of glass. The spherical shape of the particles influences the propagation of light through the cell in a characteristic fashion and results in some readily observable and rather striking consequences. Then again, the uniformity of size of the particles results in a high degree of regularity in their disposition within the cell, and this becomes conspicuously evident in the experiment.

Though the material as received shows the effects in question clearly enough, it is worth while to eliminate from it the particles deviating largely from the average size. This is effected by the aid of an appliance used in the diamond trade for sorting cut stones according to size. The device consists of a metal receptacle in two parts separated by a plate pierced by a set of circular holes. On placing the material in the upper chamber and

shaking it gently, the particles which are smaller than the rest fall into the lower chamber very quickly. The particles which are larger than the rest, on the other hand, remain in the upper chamber even after prolonged shaking. The particles which are either larger or smaller can thus be separated out from the middle fraction consisting of spherical particles having the same diameter as the circular holes in the sorter, *viz.*, one millimetre. When a cleaning up of the spheres is found to be necessary, it is readily effected by washing with strong acids and subsequently with distilled water and a final drying.

2. Some Optical Consequences of the Spherical Shape

Acetone and carbon disulphide, the two liquids used, have refractive indices respectively lower and higher than the glass for the whole range of the visible spectrum. Hence, when a cell one centimetre thick containing the spherules is filled up with either one or the other liquid by itself, the medium is incapable of regularly transmitting an incident light beam. Nevertheless, a good deal of light does find its way through the cell in these circumstances. There is, however, a remarkable difference in its appearance in the two cases. When the spherules are surrounded by a liquid of lower index, the cell presents a brilliant sparkling appearance, due evidently to the emergence of light beams of considerable intensity from localised areas on its surface. The addition of a little carbon disulphide, though insufficient to render the cell transparent to any part of the spectrum, enhances the sparkling effect and makes it more attractive by reason of a play of colours similar to the " fire " of a diamond. On the other hand, when the liquid surrounding the spherules has a higher refractive index, these effects are not observed. The emergent light is then faint and diffuse, and the cell presents a dull appearance. The striking difference between the two cases, as well as the intermediate stages in which the cell is transparent to particular regions of the spectrum, can all be simultaneously observed by pouring enough carbon disulphide to fill the lower half of the cell, and then adding acetone to fill the upper half. The acetone, being lighter, floats above the carbon disulphide and inter-diffusion takes place only slowly. The region of mixing appears as a bright band of transmitted colours, violet above and red below, while the upper and lower parts of the cell exhibit the effects arising from a penetration of the light through the cell without regular transmission.

An explanation in general terms may be readily given of the effects described above. A solid sphere surrounded by a liquid of lower index has a converging effect on a beam of light passing through it. *Per contra*,

a light beam is made divergent by the sphere, when the surrounding liquid has a higher index. The effect of passage of the light through a series of spheres would accordingly be very different in the two cases. In one case, there would be a high probability that the light would emerge from the cell with its course deviated but nevertheless having great concentrations of intensity in particular directions or at particular points on the surface of the cell. In the second case, the emergent beam would be strongly divergent and hence weak and diffuse at all points and in all directions. The correctness of this explanation can be checked by viewing a small bright source of light through the cell held in front of the eye. When the refractive index of the liquid is distinctly lower than that for the glass, the field of view surrounding the source exhibits a small number of bright spots drawn out into spectra irregularly distributed over its area. On the other hand, when the refractive index of the liquid is higher than that of glass, we observe an extended and diffuse halo exhibiting no noticeable detail.

The spherical shape of the particles has also other consequences. The deviation in the path of a ray of light by an individual sphere in the circumstances of the experiment would evidently be very small except when the ray is incident almost tangentially on the surface. Reflections of the light at the boundaries between the two media would also be of negligible intensity except in similar circumstances. Thus, the edges of the individual spheres grazed by the incident rays play a special role in determining the observed phenomena. When the cell is viewed directly, they show up as dark circles on a bright background. On the other hand, when tlhe cell is viewed obliquely, the edges appear as bright crescents of light on a dark background. The convex parts of the edges then exhibit the colours for which the liquid has the higher refractive index, while the concave parts exhibit the remaining spectral colours. Hence, when there is an equality of index at or near one end of the visible spectrum, the concave or the convex parts alone (as the case may be) of the edges appear luminous when viewed obliquely, the other parts remaining dark.

4. The Structure of the Halo

In the foregoing, for the sake of simplicity, we have used the language of geometrical optics in describing and interpreting the observed phenomena. Nevertheless, as was stressed in a recent paper in these *Proceedings*, geometric theory is wholly inadequate as a basis for an understanding of the Christiansen effect. For, we are here principally concerned with regions in the spectrum for which the particles and the surrounding liquid have nearly identical refractive indices. The smaller the difference between these

indices, the smaller would be the path-difference between the light rays traversing the cell along different routes and hence the more perfectly coherent would they be. Such coherence and the resulting regular transmission is the very essence of the Christiansen effect, and no explanation of the latter is therefore possible except on the basis of wave-optical considerations.

A study of the structure of the halo surrounding the light-source is very instructive in relation to the foregoing remarks. Remarkable changes are found to occur in the halo when by progressive additions of carbon disulphide, the refractive index of the liquid is brought into coincidence with that of the spherules successively for different parts of the spectrum. The observations may be made with a small bright source of white light or alternatively with monochromatic radiation from a mercury or sodium lamp. In the former case, the part of the spectrum for which there is equality of refractive index disappears from the coloured streaks of light seen in the field of view and appears instead in the position of the light source. Observations with a monochromatic source reveal corresponding changes in the structure of the halo. The bright spots seen in the field when the liquid has a decidedly lower index are replaced by a complicated pattern of interference streaks and then by a halo with a mottled structure consisting of a great many diffraction images of the light source. This halo contracts in area and finally vanishes when the cell becomes optically homogeneous for the wave-length employed. The regularly transmitted light which builds up in intensity during the latter stages is then at its maximum. With further additions of carbon disulphide, it diminishes in intensity and finally disappears. Simultaneously, the halo reappears and increases in its angular extension until it covers a large area and is so diffuse that no detail can be observed in it.

5. The Location of the Spherules

When the spherules of glass are placed in the cell, they naturally arrange themselves in such manner as to occupy the smallest possible volume. But the walls of the cell necessarily influence and largely determine this arrangement. For, they fix the positions of the spheres actually in contact with them and therefore also, indirectly, the positions of the spheres further out in the interior of the cell. The Christiansen experiment enables us readily to demonstrate this. For, the transparency of the cell permits us to locate the spherules, and observe their positions with respect to each other and with respect to the walls of the cell. Indeed, the influence of the shape of the cell on the disposition of the particles in its interior is strikingly evident

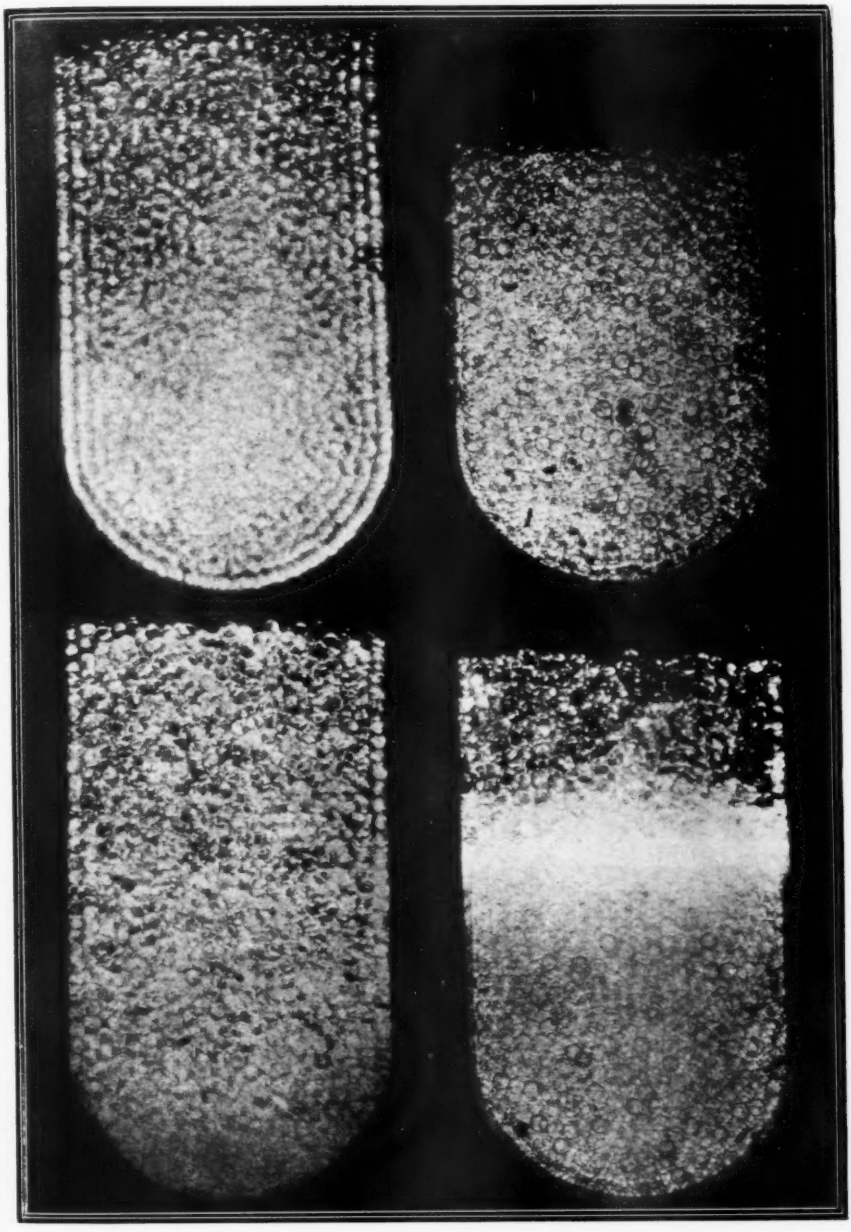

FIG. 1

FIG. 3

FIG. 2

FIG. 4

in the experiment. The layer of spherules in immediate contact with the walls naturally runs parallel to them. But their influence is observed to extend much further into the interior. At least four layers of particles running parallel to the walls of the cell may be clearly seen. This is irrespective of whether these walls are plane or curved or whether they are horizontal or vertical. When a rectangular cell is employed, five sets of such layers are observed running respectively parallel to the four walls and to the base of the cell and intersecting each other sharply along the edges of the cell.

* * * * * *

The observations reported in the present paper are obviously of a qualitative character. It is felt however, that they are of sufficient interest to justify publication. We are engaged in a more detailed study of various aspects of the experiment and hope to be able to follow up the present communication by further papers.

6. Summary

Glass in the form of tiny spheres is technically available, and by the use of a suitable appliance, the material can be sorted out so as to consist of particles of uniform size. It can then be very effectively used to exhibit the Christiansen effect. The spherical shape of the particles as well as their uniformity of size have some striking consequences which are not observed in the usual form of the experiment in which an irregular pack of powdered glass is employed. Four photographs illustrate the paper.

Description of the Figures

The photographs in Plate I illustrate the appearance of the cell in different circumstances. They represent a threefold enlargement of its actual size.

Fig. 1 exhibits the spontaneous arrangement of the spherules in layers parallel to the cell walls. Four such layers can easily be seen. The photograph was taken by transmitted light near the red end of the spectrum.

Fig. 2 exhibits the appearance of the cell when filled with acetone and held against a bright source of light.

Fig. 3 similarly exhibits its appearance when filled with carbon disulphide. Notice the numerous dark circles which represent the edges of the spheres.

Fig. 4 illustrates the effect of filling the cell with carbon disulphide below and acetone above. See the text of the paper for further details of the effects observed in this case.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XI. Conversion of Carthamidin and Isocarthamidin into Herbacetin and Tangeretin

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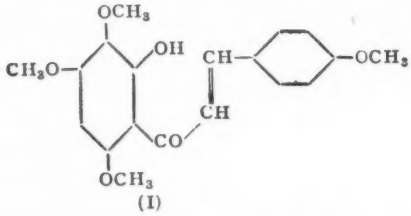
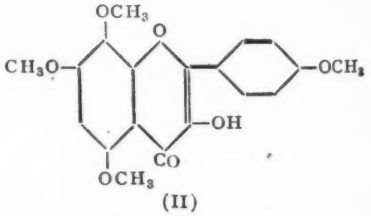
Received September 1, 1949

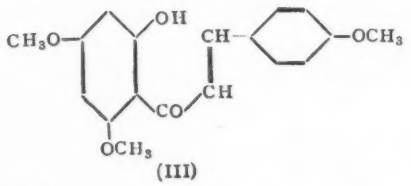
The synthesis of carthamidin and isocarthamidin has been recently reported by us.[1] A convenient method of providing confirmation of their constitution would be to convert them into the related flavonols, herbacetin and tangeretin. Earlier, Bargellini[2] reported the oxidation of 2-hydroxy-3:4:6:4′-tetramethoxy chalkone (I) (chalkone of carthamidin tetramethyl ether) by means of alkaline hydrogen peroxide to yield herbacetin tetramethyl ether (II). But more recently Geismann and Fukushima[3] have carefully investigated this reaction and have shown that when the concerned 2-hydroxy chalkone has a methoxyl group in the 6-position it gives rise predominantly to a benzal-coumaranone and only very minor quantities or nil of the corresponding flavonol is obtained. As a typical example could be mentioned the case of 2-hydroxy-4:6:4′-trimethoxy chalkone (III) which was found to produce very little of the corresponding kæmpferol derivative but formed the corresponding 4:6:4′-trimethoxy benzalcoumaranone (IV) in good yields. This reaction has been repeated by us and the result confirmed. Recently the oxidation of 2-hydroxy-3:4:6-trimethoxy chalkone to 4:6:7-trimethoxy benzalcoumaranone was reported by Balakrishna,



(I)



(II)



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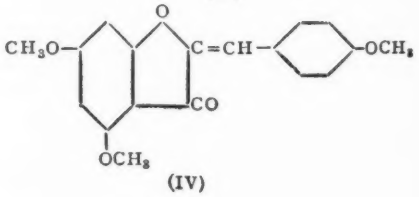
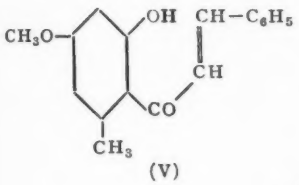


(IV)

Seshadri and Viswanath.[4] A similar change of the isomeric 2-hydroxy-4: 5: 6-trimethoxy chalkone is reported in this paper.

While discussing the mechanism of this reaction Geismann and Fukushima[3] expressed the opinion that the influence of the 6-methoxyl group is steric in nature. As a relevant example useful for this purpose 2-hydroxy-4-methoxy-6-methyl chalkone (V) having a methyl group instead of methoxyl group in the 6-position has now been prepared from orcacetophenone monomethyl ether and benzaldehyde and subjected to this oxidation. The product is insoluble in alkali and gives no colour reaction with ferric chloride showing that it is not a flavonol derivative. On the other hand its composition and reactions agree with the requirements for the benzalcoumaranone structure (VI), thus indicating that even a methyl group in the 6-position has the same effect as a methoxyl group. In this connection should be mentioned the interesting results recorded by Venkataraman and co-workers[5] that when chalkones with a free hydroxyl in the 4′-position are employed, the characteristic effect of a 6-methoxyl is not found and a flavonol is produced in the oxidation. The typical example is the formation of quercetin trimethyl ether (VII) from the dihydroxy chalkone (VIII).



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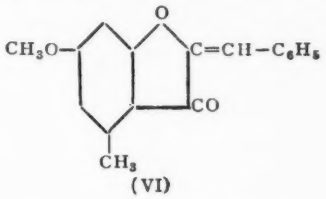
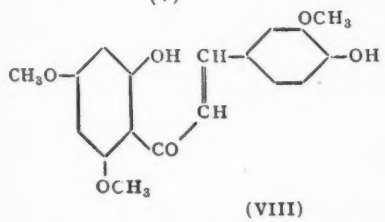
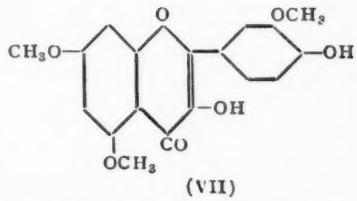


(VI)



(VIII)

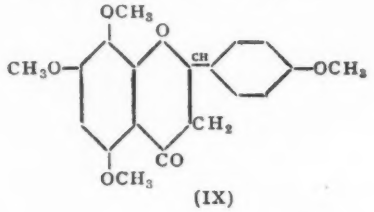


(VII)

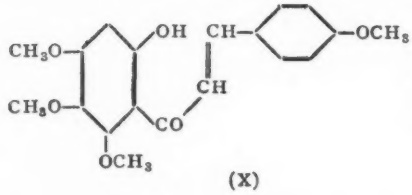
In view of the existence of possible ambiguity in Bargellini's conversion of the tetramethoxy chalkone (I) into herbacetin derivative the experiment has now been repeated. In agreement with the observation of Geismann, *et al.*, the product is found to be a benzalcoumaranone and not a flavonol derivative. However, by adopting the amyl nitrite method of Kostanecki[6] with the simplification employed by Row and Seshadri,[7] carthamidin tetramethyl ether (IX) readily yields herbacetin tetramethyl ether (II) with a free hydroxyl in the 3-position. This is quite different from the hydrogen

peroxide oxidation product and is a useful reference compound for the study of 3-glycosides of herbacetin; on methylation it yields herbacetin pentamethyl ether.

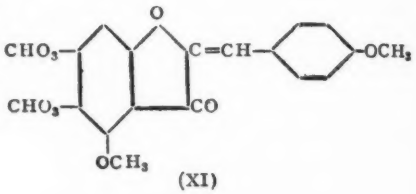
Closely analogous results have been obtained with isocarthamidin derivatives also. The chalkone tetramethyl ether[1] (X) yields the corresponding benzal coumaranone (XI) by treatment with alkaline hydrogen peroxide, whereas by treatment with amyl nitrite of the flavanone (XII) the tetramethyl ether of nor-tangeretin (XIII) is produced. This is a useful reference compound for the study of nor-tangeretin-3-glycosides and on methylation yields tangeretin.



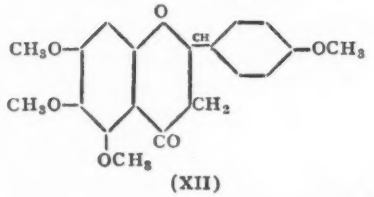
(IX) ⟶ (II)



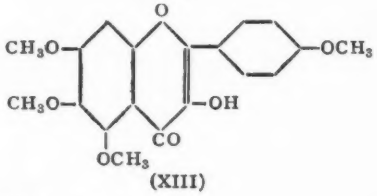
(X)



(XI)



(XII)



(XIII)

Experimental

1. *Oxidation of 2-hydroxy-4: 5: 6-trimethoxy chalkone with hydrogen peroxide*

An ice-cooled solution of 2-hydroxy-4: 5: 6-trimethoxy chalkone[1] (0·5 g.) in alcohol (5 c.c.) was treated with aqueous sodium hydroxide (5 c.c., 2 N.). To this was added an aqueous solution of hydrogen peroxide (2 c.c., 6%) in small quantities with vigorous shaking and the cooling continued for two hours. Turbidity developed slowly in the course of one hour and at the end of two hours a pale yellow crystalline powder separated. The mixture was diluted with water (10 c.c.) and extracted with ether. On

evaporating the ether solution a sticky yellow solid was obtained. It crystallised from alcohol in the form of yellow tiny prisms melting at 142–43°. It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution. With concentrated sulphuric acid it gave a deep red colour. It thus had all the properties required for 4: 5: 6-trimethoxy benzalcoumaranone. Yield 0·25 g. (Found: C, 68·8; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69·1; H, 5·1%.) Acidification of the alkaline solution gave no product.

2. *2-Hydroxy-4-methoxy-6-methyl chalkone (V): Preparation*

A mixture of 4-O-methyl-orcacetophenone (1 g.) and benzaldehyde (3 c.c.) was dissolved in alcohol (20 c.c.) and sodium hydroxide solution (3 g. in 3 c.c. water) added with cooling under the tap. The flask was corked air tight and kept at room temperature for 48 hours. It was then diluted with water (50 c.c.) and extracted with ether to remove excess of benzaldehyde and acidified with concentrated hydrochloric acid. The chalkone that separated was extracted with ether and the ether solution washed with aqueous sodium bicarbonate. On distilling off ether a yellow sticky solid was obtained. It crystallised from alcohol as yellow prisms melting at 125–27°. It gave a brown colour with ferric chloride in alcohol and dissolved in aqueous sodium hydroxide. Yield 0·7 g. (Found: C, 75·9; H, 6·3; $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%.)

3. *Oxidation with hydrogen peroxide*

To a solution of the above chalkone (0·5 g.) in alcohol (10 c.c.) sodium hydroxide (5 c.c., 10%) was added and the solution cooled in ice. Hydrogen peroxide (2·5 c.c., 6%) was slowly added little by little with shaking and the product worked up just as in experiment (1). It crystallised from dilute alcohol in the form of pale yellow tiny prisms melting at 136–38°. It gave a deep red colour with conc. sulphuric acid and was insoluble in aqueous alkali. Its alcoholic solution gave no colour with ferric chloride. Thus its properties agreed with the requirements of 4-methyl-6-methoxy benzalcoumaranone (VI). (Found: C, 76·4; H, 5·6; $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%.)

4. *Oxidation of 2-hydroxy-3: 4: 6: 4′-tetramethoxy chalkone (I)*

A solution of the chalkone[2] (1 g.) in alcohol (20 c.c.), sodium hydroxide solution (10 c.c., 10%) and hydrogen peroxide solution (5 c.c., 6%) were employed and the product worked up as described in the above experiments. 4: 6: 7: 4′-Tetramethoxy-benzalcoumaranone crystallised from alcohol in the form of bright yellow rhombohedral prisms melting at 200–01°. Yield 0·5 g. It gave a deep red colour with concentrated sulphuric acid. It was insoluble in aqueous alkali and gave no colour with ferric chloride in

alcoholic solution. (Found: C, 66·7; H, 5·7; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.)

The aqueous alkaline solution left after the complete removal of the benzal coumaranone was acidified with concentrated hydrochloric acid and extracted with ether. On evaporating the ether solution a small quantity of a colourless solid was obtained. It dissolved completely in aqueous sodium bicarbonate and was identical with anisic acid.

5. *Preparation of* 5: 7: 8: 4′-*tetramethoxy*-3-*hydroxy flavone* (*II*)

5: 7: 8: 4′-Tetramethoxy flavanone[2] (IX), m.p. 152–54° (1 g.), was dissolved in alcohol (40 c.c.) and the solution kept gently boiling over a small flame. Amyl nitrite (3 c.c.) and fuming hydrochloric acid (20 c.c., d. 1·19) were added alternately little by little with continuous stirring. After the addition, the mixture was allowed to stand for two hours with occasional shaking. It was then diluted with water (150 c.c.) and the solid product filtered and washed with water. Yield 0·3 g. A further small quantity was obtained by ether extracting the acid solution. The ether solution was extracted with aqueous sodium hydroxide and the alkaline solution on acidification gave the hydroxy-flavone. Total yield 0·35 g. On crystallisation from alcohol, 3-hydroxy-5: 7: 8: 4′-tetramethoxy flavone was obtained as bright yellow rectangular rods and needles melting at 198–200°. It dissolved readily in aqueous alkali and formed a sparingly soluble sodium salt in concentrated solution. It gave a reddish brown colour with alcoholic ferric chloride. When reduced in alcoholic solution with magnesium and hydrochloric acid an orange red colour was developed. With concentrated sulphuric acid it formed a yellow solution with a green fluorescence. (Found: C, 64·0; H, 4·7; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.) A mixture of this substance with the product of experiment (4) melted below 160°.

6. *Methylation*

The above 3-hydroxy flavone (0·3 g.) was refluxed in acetone solution with dimethyl sulphate (0·1 c.c.) and anhydrous potassium carbonate (0·5 g.) for 6 hours. It was then filtered and the potassium salts washed with hot acetone. On distilling off acetone a pale yellow solid was obtained. It crystallised from dilute alcohol as colourless rectangular rods and needles melting at 155–56°. It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcohol. It agreed in its properties with herbacetin pentamethyl ether[8] and a mixed melting point with an authentic sample was undepressed.

7. *Ethylation* (*Preparation of* 3-*ethoxy*-5 : 7 : 8 : 4′-*tetramethoxy flavone*)

3-Hydroxy-5 : 7 : 8 : 4′-tetramethoxy flavone (0·2 g.) was dissolved in acetone (20 c.c.), ethyl iodide (0·2 c.c.) and anhydrous potassium carbonate (1 g.) were added and the mixture refluxed for 6 hours. Acetone was then distilled off and the residue treated with water and extracted with ether. On evaporating the ether solution 3-ethoxy 5 : 7 : 8 : 4′-tetramethoxy flavone was obtained as a pale yellow solid. It crystallised from dilute alcohol in the form of almost colourless clusters of needles and melted at 97–98°. It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution. When reduced with magnesium and hydrochloric acid its alcoholic solution gave a scarlet red colour. With concentrated sulphuric acid it gave a yellow solution without any fluorescence. (Found: C, 65·3; H, 5·5; $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%.)

8. *Oxidation of* 2-*hydroxy*-4 : 5 : 6 : 4′-*tetramethoxy chalkone* (*X*)

This chalkone,[1] on treatment with hydrogen peroxide as described in the above experiments, gave 4 : 5 : 6 : 4′-tetramethoxy benzalcoumaranone (XI) in 50% yield. It crystallised from alcohol in the form of stout yellow rectangular rods melting at 189–90°. Its colour reactions were similar to those already described. (Found: C, 66·3; H, 5·6; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.) The aqueous solution left after removing the benzalcoumaranone on acidification gave a small quantity of anisic acid.

9. 3-*Hydroxy*-5 : 6 : 7 : 4′-*tetramethoxy flavone* (*XIII*)

To a gently boiling solution of isocarthamidin tetramethyl ether[1] (XII) (1 g.) in alcohol (40 c.c.) were added alternately amyl nitrite (3 c.c.) and concentrated hydrochloric acid (20 c.c., d. 1·19) little by little with stirring. After the addition, the mixture was left for two hours with occasional shaking; a bright yellow solid separated gradually. It was then diluted with water (100 c.c.) and the solid product filtered and washed with water. On working up the aqueous solution as described in a previous experiment some more of the product could be isolated. It was twice crystallised from alcohol when the flavonol was obtained as bright yellow rhombic plates melting at 171–73°. It dissolved in aqueous alkali easily and gave a dark brown colour with ferric chloride in alcohol. With concentrated sulphuric acid it gave a yellow solution with a green fluorescence. Yield 0·35 g. (Found: C, 63·7; H, 5·0; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.)

10. *Methylation*

The above 3-hydroxy compound (0·2 g.) was methylated with dimethyl sulphate (0·1 c.c.) and anhydrous potassium carbonate (0·5 g.) in dry acetone, by refluxing for 6 hours. The mixture was then filtered and the

potassium salts washed with hot acetone. On distilling off acetone a pale yellow solid was obtained. It crystallised from alcohol in the form of colourless rectangular plates melting at 153–54°. It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcohol. It agreed in its properties with tangeretin[9] and the mixed melting point with a sample of tangeretin was undepressed.

Summary

A convenient method of providing confirmation of the constitution of carthamidin and isocarthamidin is to convert them into herbacetin and tangeretin. The earlier claim of Bargellini to have prepared herbacetin tetramethyl ether by the oxidation of 2-hydroxy-3 : 4 : 6 : 4′-tetramethoxy chalkone with alkaline hydrogen peroxide could not be supported. This reaction yields the corresponding benzalcoumaranone and not flavonol in agreement with the behaviour of analogous and simpler chalkones having a methoxyl group in the 6-position. An example is described where even a methyl group in that position brings about the same result. However by the action of amyl nitrite and hydrochloric acid carthamidin and isocarthamidin tetramethyl ethers yield the corresponding flavonol derivatives.

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Addendum

After this communication had been written up we received the papers of Oliverio,[10] *et al.*, dealing with the hydrogen peroxide oxidation of chalkones I and X and related members. They have considered the products to be flavonols, but have not recorded their ferric reaction or alkali solubility. They seem to be unaware of the work of Geismann and Fukushima and the possibility of the products being benzalcoumaranones. Their preparations are therefore not free from ambiguity and they differ in their properties from ours.

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ON THE REFLECTION OF ATMOSPHERICS FROM THE IONOSPHERE AT NIGHT—PART II

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Introduction

In a previous communication[3] an account of the work done on the reflection of atmospherics from the ionosphere at night at Poona was given. Following Laby and his co-workers,[4,5] the records of the waveforms of atmospherics obtained with a self-triggering cathode-ray oscillograph were utilised to obtain in some typical cases such information as the height and reflection coefficient of the ionosphere, the distance of the sources of atmospherics, etc. In this paper are described and discussed the results of further investigations.

Experimental

Excepting a few minor changes in the electronic circuits, such as the introduction of a higher H.T. supply to the accelerating electrodes of the cathode-ray oscillograph, a more critical balancing of the 50 cycles suppressor unit, etc., which were found necessary by experience, the experimental arrangement described earlier was employed throughout these investigations. The necessary calibrations were carried out from time to time and were taken into account while reducing the different records.

Results

Plates II and III show some of the typical records of the waveforms of atmospherics obtained at Poona. The results of calculations based on the measurements of all such records are given in Tables I, II and V. Table I gives the data for the first 50 atmospherics out of a total of 388 atmospherics obtained during the periods August to November of 1944 and August to October of 1945. The first two columns of this table give the date and atmospheric number respectively. The third and fourth columns give respectively the height of the ionosphere and the distance of the origin of the atmospherics as calculated from the following formulæ based on the reflection theory of the waveforms of atmospherics first put forward by Laby.[4,8]

$$h = \frac{c}{2}\sqrt{\frac{T_1 T_2 (T_1 + T_2)}{(r^2 - q^2) T_1 - (q^2 - p^2) T_2}}, \qquad (1)$$

where h is the height of the ionosphere, c, the velocity of light, p, q and r, the orders of the reflected sky pulses, T_1, the time interval between the qth and pth pulses and T_2, that between the rth and qth pulses. And

$$d^2 = \frac{R}{R+h}\left[\left\{\frac{4h^2(q^2-p^2)-c^2T^2_1}{2cT_1}\right\}-4h^2p^2\right], \qquad (2)$$

where d is the distance of the source of atmospheric and R, the radius of the earth.

The fifth column shows the duration of the first pulse while the sixth column gives the maximum number of identifiable sky pulses. The seventh column gives the mean reflection coefficient as defined by Watson-Watt,[9] Schonland and others,[8] and deduced from the actual measurements of the amplitudes of the successive sky pulses. The reflection coefficient r_i is given by $r_i \geqslant \sqrt[p]{\frac{A_{n+p}}{A_n}}$, where A_n and A_{n+p} are the amplitudes of the nth and $(n+p)$th sky pulses, respectively. The data given in the full table of 388 atmospherics form the basis of the discussion in this paper. The monthly averages of the height and the reflection coefficient of the ionosphere obtained from the above table are given in Tables III and IV. Similarly, the frequency distributions of the various quantities deduced are shown graphically in Figs. 1 to 5.

Table II is a test table and shows the applicability of the multiple reflection theory and the formula based on it for the deduction of the height of the ionosphere.

Table V gives some characteristic measurements of a few well recorded precursors.

Discussion of Records

Plates II to IV show typical examples of waveforms of atmospherics obtained at night at Poona. Plate IV also contains a few waveforms obtained during the daytime [(1) to (4)]. Some of the records in Plate II show more or less the ideal waveform described earlier, *i.e.*, one which shows first the precursor, then the ground pulse and finally a series of sky pulses of diminishing amplitude [(1), (2), (9), (10), (13), (14)]. It should be noted here, that it is not always possible to obtain such ideal waveforms in all the atmospherics. The recording device to some extent, is also responsible for this. Because, if the field strength, for instance, of the first portion of the precursor is not sufficiently large the cathode-ray oscillograph beam is not switched on until the arrival of a sufficiently large component of the precursor (which may come at any time) and the record is obtained from that instant onwards.

Naturally such records will show a part of the precursors or not show them at all [Plate II, Nos. (3) to (8), (11) and (12)]. When the cathode-ray oscillograph beam is switched on by the arrival of the ground pulse itself, the record begins with the ground pulse. (Strictly speaking without its small preliminary portion) [Plate III, Nos. (1) to (5)]. On several occasions, two different atmospherics arriving almost simultaneously or in quick succession at the place of observation were recorded as superposed traces [Plate III, Nos. (6), (7)]. The beam switched on by the first was useful if the second happened to be weak. Precursors were observed only in less than 10% of the waveforms recorded here. Similarly in England, Lutkin[6] found them in about 15% and 17% of the records at Slough and Leuchars respectively.

None of the daytime atmospherics had this typical wave form and as mentioned before, even at night all atmospherics do not show it and cannot therefore be used in this way to obtain ionospheric information [see Plate IV, Nos. (10) to (13)]. They are too distorted or there is too much superposition. Records (15) and (17) were obtained during heavy rain in the neighbourhood. Some of the complex waveforms whose number is certainly not small have to be taken into account while making a statistical study [Plate IV, Nos. (5) to (14), (16) and (18)].

Discussion of the Results of Calculations

In all, 206 and 182 waveforms were utilised from the records of 1944 and 1945 respectively. They are considered here to form one single random sample and analysed statistically.

(1) *The height of the ionosphere.*—The value of this lies generally between 70 km. and 110 km. with a maximum at 90 km. (Fig. 1). The mean of the whole sample is 91·5 km. The probable error, the mean error and the standard deviation are 3·7, 5·6 and 24·3 km. respectively. Both the distribution and the mean are in general agreement with what others have obtained by this method. Laby and co-workers in Australia obtained about a dozen values lying between 53 km. and 82 km. with a mean at 73 km. From observations during two winter months Schonland and co-workers in South Africa obtained values lying between 85·5 km. and 90·5 km. with a mean at 88 km. It should be pointed out here that the values of height deduced from these measurements may be expected to be smaller than those obtained by the variable frequency methods usually employed in the ionospheric investigations. It may be mentioned regarding Table I that in the majority of cases the height of the ionosphere has been determined from the triad (3, 6, 9), *i.e.*, from the time interval T_1 between the 6th and the 3rd sky pulses and T_2 between 9th and 6th sky pulses. Only

a small number of cases (about 20 in all) in which only 5 or 6 sky pulses could be seen clearly, the triad (1, 2, 3) has been used. Table II is a test-table in which more than one triad were used to calculate the height of the ionosphere. It shows the constancy of h to within $\pm$ 3 km. about the mean value.

No systematic variation in the average monthly height of the ionosphere is observed in these investigations (Table I).

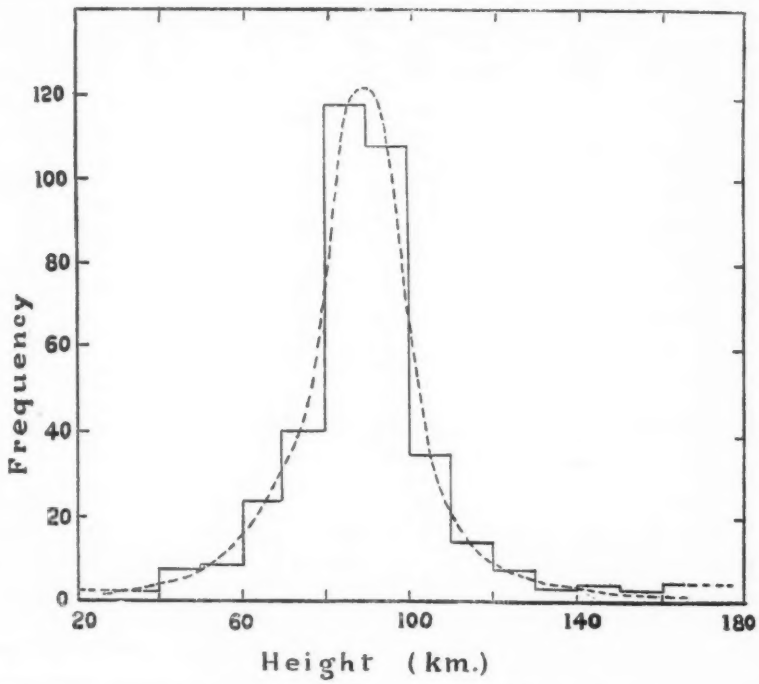

FIG. 1. Frequency distribution of the height of reflection

In Fig. 7 the height of the reflecting layer is plotted against the distance of the source of the atmospheric derived for the same atmospheric. In spite of the scatter of points, a general trend as indicated by the curve seems to exist. There appears to be no definite correlation between the height and the reflection coefficient of the ionosphere obtained from the same atmospheric. One important point to which attention may be drawn here is that on a few nights, surprisingly small (the lowest being about 25 km.) and surprisingly large heights (the highest being about 285 km.) were also obtained.

(2) *The distance of the origin of atmospherics.*—The distance of the origin of atmospherics received at night in general lies between 300 km. and 900 km. though some have been received from distances greater than 2000 km. At Poona they come most frequently from 400-800 km. (Fig. 2).

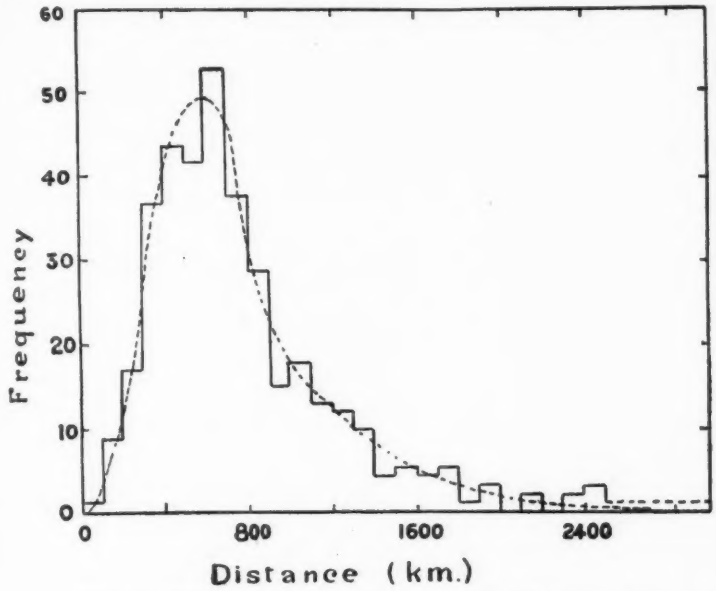

FIG. 2. Frequency distribution of the distance of atmospherics

(3) *The number of sky pulses.*—In general about 10 to 15 sky pulses were observed clearly. But in some cases as many as 40 could be counted. They may be seen in some of the photographic reproductions in Plates II and III. When the number of reflections is plotted against the duration of the main pulse and the reflection coefficient, in spite of some scatter of the points the number of reflections at first increases slowly but later more rapidly both with the duration of the main pulse and the reflection coefficient.

(4) *Reflection coefficient of the ionosphere.*—The reflection coefficient varies from 0·60 to 0·95 and has a most common value of 0·80 (Fig. 4). Very large values near 0·95 are particularly surprising when it is remembered that it is the mean value obtained with at least three or four reflections at the ionosphere and two or three at the ground. Schonland obtained values exceeding 0·80 for the larger pulses. However, there appears to exist no significant correlation between the reflection coefficient of the ionosphere and the duration of the main pulse observed here.

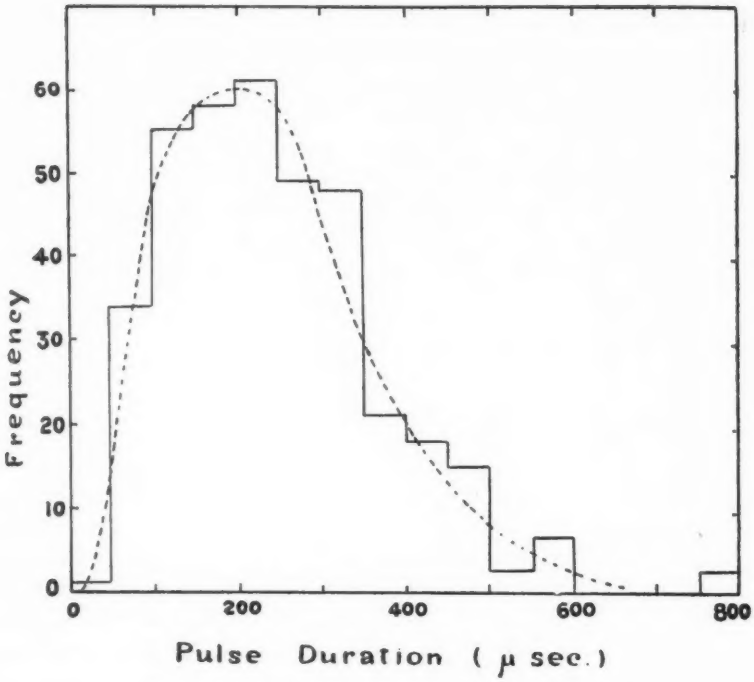

FIG. 3. Frequency distribution of the pulse duration

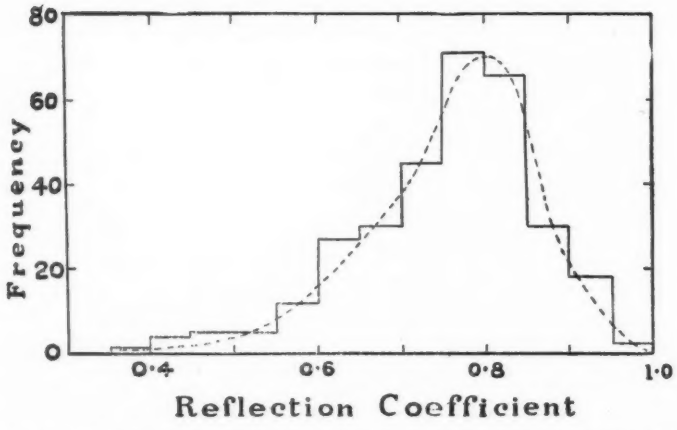

FIG. 4. Frequency distribution of the reflection coefficient of the ionosphere

(5) *The duration of the main pulse.*—The frequency distribution of the duration of the main pulse shows that it lies between 50 micro-secs. and 350 micro-secs. 200 micro-secs. represents the most common value. Values larger than 600 micro-secs. and smaller than 50 micro-secs. are particularly absent. If these values are taken to represent half-cycles, they correspond to frequencies of 0·17 kcs./sec. and 20 kcs./sec. respectively. The duration of pulses observed by Appleton,[1,2] Watson-Watt[9] and others also range from about 50 to 600 micro-secs. Schonland[8] and others obtained values ranging from 50 to 400 micro-secs. It should be pointed out here that pulse durations larger than 400 micro-secs. which are probably caused by the interference effects of the subsidiary discharges in the lightning channel have definitely been observed here (Fig. 6).

(6) *The nature of pulses.*—Some of the more common types of pulses observed here are sketched in Fig. 6. Both the positive and negative forms, *i.e.*, those obtained by the mirror image in the time axis occur. Only one of them is traced for convenience. All these forms are similar to some of the numerous forms traced by Watson-Watt and others.[9,1,2] Two points may be noted here. The first two rows show simple (and perhaps basic forms) while the third and fourth rows show complicated forms which are supposed here to be produced by quick succession of smaller pulses due to oscillatory discharges which follow the main return stroke in the lightning channel. They may also be due to the horizontal portions of the lightning flash. The second point is that these forms of pulses are not maintained intact in all the sky reflections. This behaviour is often referred to as " the phase change of the pulse". This is partly to be ascribed to the interference of the different subsidiary pulses coming along different paths and thus arriving at the place of observation at different epochs. Both these points can be seen by a careful examination of some of the records reproduced here.

(7) *The field changes.*—It is interesting to study the field changes both with regard to the direction and magnitude of the first movement of the oscillographic spot due to the arrival of the main pulse. Although in many cases (133 out of 388 or 34%) the sign was doubtful, of the remaining 255 wave-forms 206 (81%) showed a negative field change, while only 49 (19%) showed a positive change. There is on the whole a considerably greater frequency of the destruction of negative cloud moment than of positive moment. Lutkin[6] also finds that in about 80% of the lightning flashes occurring in England negative cloud moment is destroyed. He further states " in storms of the local type, destruction of the negative cloud moments accounts for almost all flashes while in the storms of the ' frontal ' type positive moments are destroyed as frequently as the negative ones".

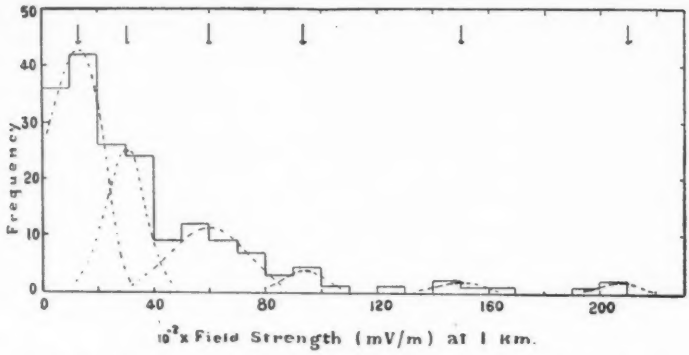

FIG. 5. Frequency distribution of the field strength at 1 km. distance from the source of atmospherics

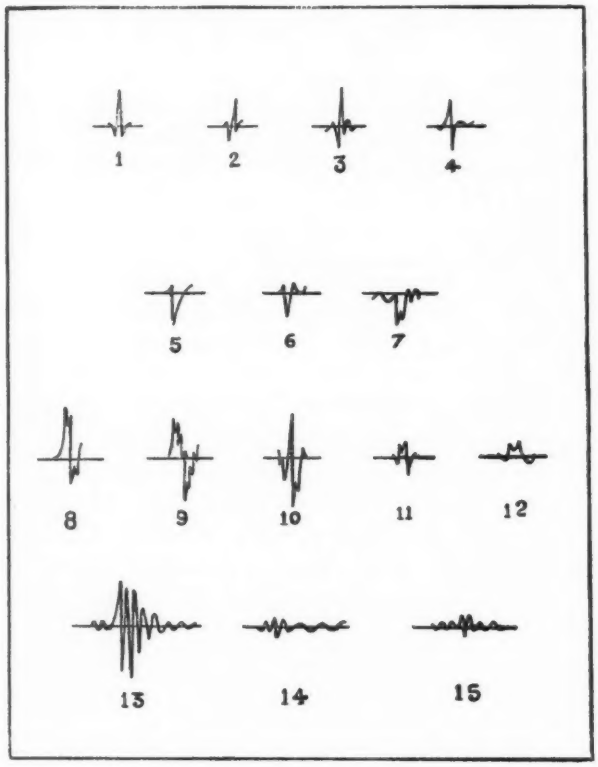

FIG. 6. Some forms of pulses

(8) *The field strength.*—The frequency distribution of the field strength reduced in about 180 cases (values not included in Table I) for a distance of one km. from the source of atmospherics is shown in Fig. 5.

(9) *The peak power of an atmospheric.*—By analogy with the power required in a wireless transmitter situated on the ground to produce a field strength E, the power radiated by a lightning flash can be expressed as: $P = (Ed/300\phi)^2$, where P is the power radiated in KW, d, the distance of the source of atmospheric in km.; E, the field strength measured in mV./m.; and ϕ, the Sommerfeld factor which allows for the curvature of the earth's surface

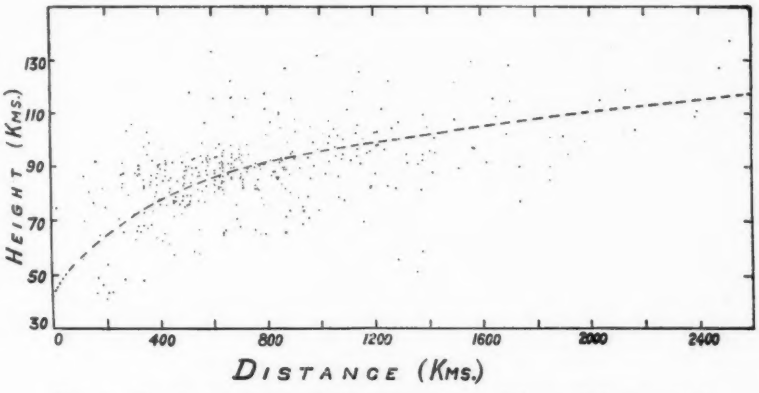

FIG. 7. Graph showing the relation between the distance of the source of atmospheric and the height of the reflecting layer

and finite conductivity of the ground. For the distances and pulses considered here the value of ϕ is unity. Also the effect of the inductive field will be unimportant for the large distances and long waves considered here. Peak power was calculated for about a dozen values of the field strength and distances measured here. It was found to vary between 10^5 to 10^7 KWs. (Table VI). The effective height of the lightning channel as a radiating aerial was also calculated from the formula

$$H = \frac{Ed\lambda}{0{\cdot}377\,I} \cdot e^{0{\cdot}0015\frac{d}{\sqrt{\lambda}}}$$

where H is the effective height in km.; E, the field strength in V./m.; d, the distance of the source of atmospheric; λ, the wavelength of the radiated pulse in km.; and I, the current in the discharge channel in amperes (assumed to be 3000 amps. after Goodlet, the same as that used by Laby and others). H was found to vary between 400 m. and 2000 m. (Table VI).

(10) *Precursors.*—With a view to find any possible connection between the physical processes which produce the precursors as distinct from the main pulse of an atmospheric and their oscillographic records all records with precursors were carefully examined. Data especially based on clear traces of both the precursors and the main pulse are given in Table V. It contains such quantities as the total duration of the precursor, duration of the main pulse, the time interval between the end of the precursor and the beginning of the main pulse, approximate number of half-cycles in the precursors and the maximum amplitude in the precursor. There does not, however, seem to exist any general relationship amongst the quantities considered. This interpreted in terms of the mechanism of a lightning discharge as elucidated by the work of Schonland and his co-workers[7] shows that there exists no relation between the main flash in the channel and the dart-like and step-wise advances of the ionised air which produces the main conducting channel.

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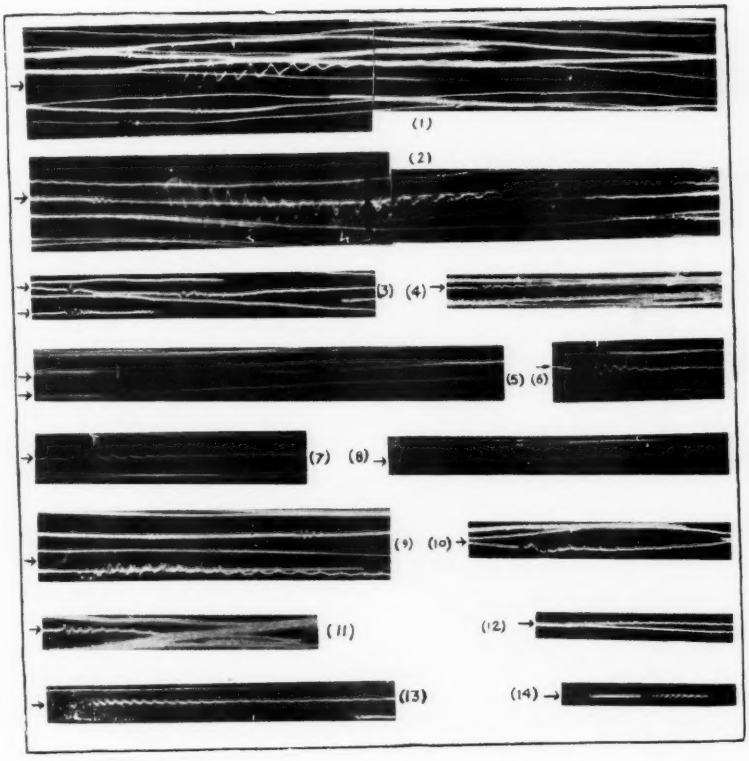
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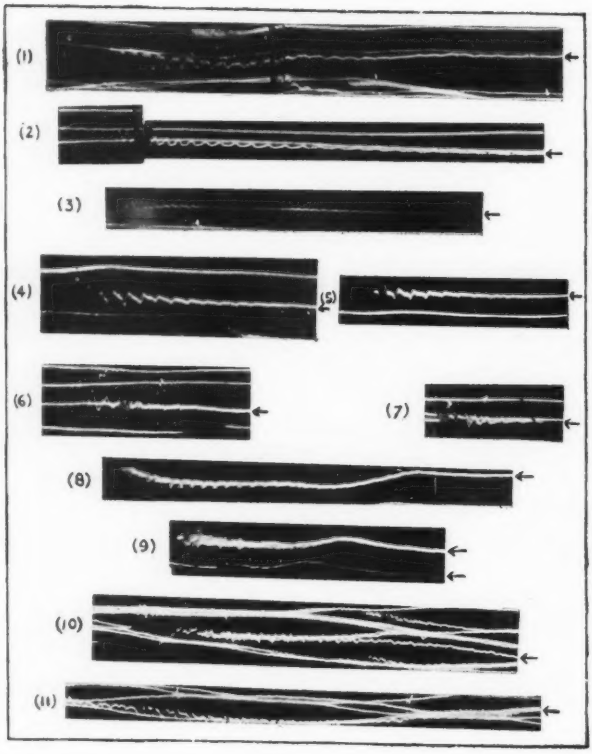
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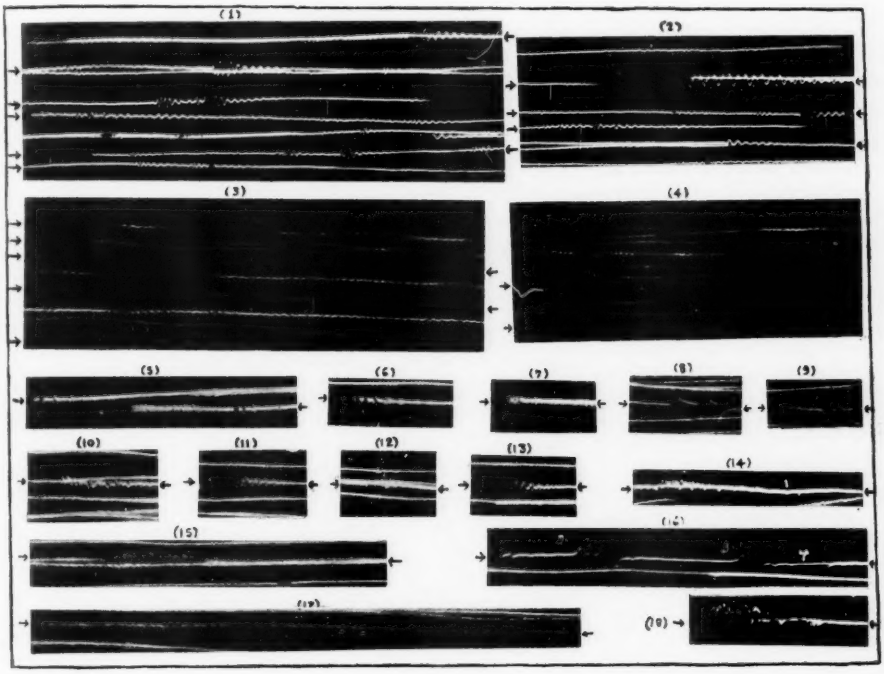
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APPENDIX

TABLE I

Data for 1944 *and* 1945

Date (i)	Atmospheric number (ii)	Height of reflecting layer (km.) (iii)	Distance of origin of atmospheric (km.) (iv)	Duration of the first pulse (μ sec.) (v)	Number of reflections (approx.) (vi)	Reflection coefficient (vii)
5—8—1944 ..	1	81	145	565	33	0·79
do ..	4	70	125	300	15	0·58
do ..	5	59	1378	170	10	..
6—8—1944 ..	1	88	272	230	13	0·91
do ..	2	78	1069	580	37	0·93
do ..	4	94	586	360	16	0·85
do ..	5	94	705	360	9	0·60
do ..	6	91	673	180	9	0·60
7—8—1944 ..	1	81	440	200	18	0·86
do ..	2	235	10350	340	9	..
do ..	4	115	2539	250	9	..
do ..	5	96	1432	180	11	..
18—8—1944 ..	2	..	..	150	10	..
do ..	3	51	1358	250	14	0·83
do ..	4	89	1421	500	15	..
5—9—1944 ..	1A	95	361	230	15	0·71
do ..	1B	76	431	285	23	0·81
do ..	2B	56	1291	320	40	0·76
do ..	3B	81	608	570	18	0·90
6—9—1944 ..	1A	88	553	575	23	0·80
do ..	2A	95	733	400	10	0·73
do ..	3A	54	498	580	12	0·48
do ..	5A	84	857	470	18	0·83
do ..	6A	71	674	425	20	0·81
do ..	7A	99	1216	330	9	..
do ..	8A	81	889	400	10	0·81
do ..	9A	75	205	310	9	0·72
do ..	1B	150	4536	240	22	0·81
do ..	2B	101	1430	280	12	0·75
do ..	3B	148	3966	400	9	0·69
do ..	4B	25(?)	..	280	10	0·76
8—9—1944 ..	1	93	909	205	13	..
do ..	2	88	1025	..	11	..
do ..	3	77	1746	190	15	0·49
do ..	4	100	1139	345	13	0·75
do ..	5	103	803	200	10	0·68
do ..	6	164	4400	300	15	0·80
do ..	7	85	422	230	10	0·79
9—9—1944 ..	1	78	489	485	36	0·82
do ..	2	94	858	300	10	0·69
do ..	3	71	1164	270	18	0·88
do ..	5	56	123	350	20	0·80
10—9—1944 ..	1A	84	270	415	17	0·83
do ..	4	87	126	265	19	0·71
do ..	4A	79	383	170	10	0·81

TABLE I—(*Contd.*)

Date (i)	Atmospheric number (ii)	Height of reflecting layer (km.) (iii)	Distance of origin of atmospheric (km.) (iv)	Duration of the first pulse (μ sec.) (v)	Number of reflections (approx.) (vi)	Reflection coefficient (vii)
10—9—1944 ..	5B	101	1171	130	11	0·66
do ..	7	90	868	240	14	0·86
do ..	2	77	457	220	18	0·79
do ..	3	76	787	345	40	0·79
do ..	11	76	694	240	13	0·83
do ..	13	92	1368	220	20	0·83
do ..	15	97	1188	240	13	0·78
do ..	14	83	626	240	9	0·72
do ..	10	72	456	310	10	0·90

TABLE II

Test for constancy of H by the triad formula

Number and date of the atmospheric	Time I.S.T.	Triad (p, q, r)	Height in km.	Mean height in km.
2 6—8—1944 ..	2100-2115	1,2,3	76·6	77·2
		3,6,9	77·8	
2A 6—9—1944 ..	1900-2000	4,5,6	91·8	93·6
		3,6,9	95·5	
3 6—9—1944 ..	1900-2000	1,2,3	92·4	90·4
		2,3,4	89·0	
		4,5,6	93·0	
5 14—9—1944 ..	2200-2300	1,2,3	87·9	86·9
		3,6,9	85·8	
6 15—9—1944 ..	2245-2300	1,2,3	82·4	82·3
		3,6,9	82·3	
11 15—9—1944 ..	2245-2300	3,4,5	135·6	140·9
		3,6,9	146·3	
1 17—9—1944 ..	2000-2015	1,2,3	70·6	69·7
		3,6,9	68·8	
7 17—9—1944 ..	2000-2015	1,2,3	84·2	82·4
		2,3,4	80·6	
8 17—9—1944 ..	2000-2015	1,2,3	76·4	75·9
		2,3,4	74·3	
		3,6,9	77·1	
6 18—9—1944 ..	2000-2100	2,3,4	84·0	83·3
		3,4,5	80·7	
		4,5,6	82·9	
		3,6,9	85·5	
1 30—9—1945 ..	2130-2140	3,6,9	98·1	95·6
		9,12,15	93·1	
3 30—9—1945 ..	2130-2140	3,6,9	94·9	95·7
		9,12,15	95·6	
2 8-10—1945 ..	2400-0050	3,6,9	98·8	95·6
		9,12,15	92·4	
1 15-10—1945 ..	2100-2115	3,6,9	94·6	96·9
		9,12,15	99·1	
1 19-10—1945 ..	2000-2045	3,6,9	89·0	93·1
		8,10,12	97·2	
4 19-10—1945 ..	2000-2045	3,6,9	93·3	92·5
		8,10,12	91·7	
6 19-10—1945 ..	2000-2045	3,6,9	90·3	94·0
		8,10,12	97·7	
7 19-10—1945 ..	2000-2045	3,6,9	97·4	96·9
		8,10,12	96·4	

TABLE III

Monthly mean values of the height of the reflecting layer during 1944 *and* 1945

Mean height using all observations = 91·5 km.

Year / Month	1944		1945	
	Height km.	Number of observations	Height km.	Number of observations
May ..	..	..	95·3	3
..	..	..	..	..
August ..	94·5	14	93·2	17
September ..	91·0	106	91·4	56
October ..	85·3	36	92·7	100
November ..	91·8	50	..	..

TABLE IV

Monthly mean values of the reflection coefficient of the ionosphere during 1944 *and* 1945

Mean reflection coefficient using all observations = 0·76

Year / Month	1944		1945	
	Reflection coefficient	Number of observations	Reflection coefficient	Number of observations
May ..	..	..	0·70	3
..	..	..	..	..
August ..	0·77	9	0·82	15
September ..	0·76	95	0·77	38
October ..	0·79	29	0·70	92
November ..	0·78	35	..	..

TABLE V

Data about the precursors obtained from some typical records of 1945

Date	Time	Atmospheric No.	Total duration in micro-secs.	No. of half cycles (approx.)	Average time of half-cycle, in micro-secs.	Average ratio of successive amplitudes	Maximum amplitude in the precursor	Amplitude of ground pulse	Interval between ground pulse and precursor, in micro-secs.
2—8—1945	2040-2045	1	1000	30	30	1·5	7·0	7·0	550
do	do	2	800	50	16	1·3	4·0	1·6	150
do	do	3	5000	200	25	1·4	9·0	1·6	150
21—8—1945	2030-2035	1	1600	200	8	1·6	2·1	3·8	500
25—8—1945	2130-2200	1	3600	100	36	1·2	3·0	4·8	100
do	do	2	4000	75	54	1·2	4·9	5·1	5000
8-10—1945	2000-2030	1	1600	50	32	1·75	2·0	4·2	Nil
13-10—1945	2100-2115	1	8000	100	80	..	2·0	..	Nil
do	do	2	600	50	12	..	4·0	..	550
do	do	4	4000	100	40	..	4·8	..	550
14-10—1945	2100-2130	1	2000	200	10	..	13·0	..	Nil
15-10—1945	2030-2045	1	6000	500	12	1·2	9·1	5·6	1500

TABLE VI

Radiated peak-power and effective height of a lightning discharge

Date	Atmospheric No.	Peak-power radiated KW	Effective height H in m.
5—9—1944	IA	$1·14 \times 10^5$	650
do	3B	$10·9 \times 10^5$	5000
13—9—1944	3	$11·5 \times 10^5$	2000
25—9—1944	3	$4·3 \times 10^5$	1700
13-10—1944	1	$108·5 \times 10^5$	640
19-10—1944	8	$50·4 \times 10^5$	580
6-11—1944	1	$30·4 \times 10^5$	680
27—8—1945	4	$64·0 \times 10^5$	420
6—9—1945	4	$4·4 \times 10^5$	510
19-10—1945	4	$30·6 \times 10^5$	470

STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXIV. The Camphor-β-sulphonates (*d*-, *l*-, and *dl*) of *o*-, *m*-, and *p*-, Anisidine and of *o*- and *p*- Aminophenol

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In Parts XXVIII and XXIX of this series of investigations,[1] the rotatory dispersion of salts of camphor-β-sulphonic acid (*d*-, *l*-, and *dl*-) were described. We have included in the present investigation the salts of *o*-, *m*- and *p*-anisidine and *o*- and *p*-aminophenol. One of the objects of the work is to study the effect of substituting the methoxy and hydroxy groups in different positions for an hydrogen atom in the benzene ring of the anilino camphor-β-sulphonates on the rotatory power of the resulting compounds.

Nature of the Rotatory Dispersion

These compounds exhibit simple rotatory dispersion as their rotatory powers can be expressed by Drude's one-term equation. The calculated values of the rotatory power for different wavelengths agree with the observed ones within the limits of experimental error. The Tables (IV to VIII) record the observed values of rotatory dispersion of the *d*-, and *l*-compounds. The individual calculated values are omitted owing to economy of space. Out of 480 observations, 472 measurements are within the limits of experimental error, namely 0·02° in the observed angle of rotation.

The Physical Identity of Enantiomers

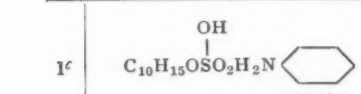
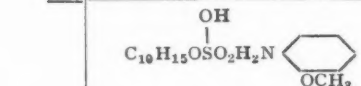
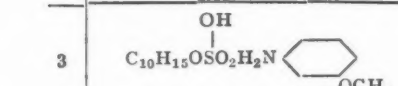
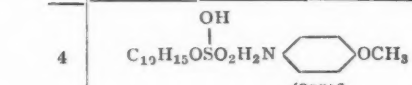
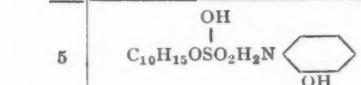
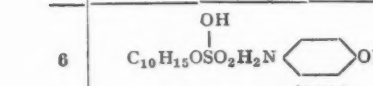
The rotatory powers of *d*-, and *l*-forms of the salts of camphor-β-sulphonic acid are identical in all solvents and this lends further support to Pasteur's Principle of Molecular Dissymmetry. Out of 480 observations recorded in this paper, in as many as 434 cases, the differences in the numerical values of the specific rotatory power of the optically active and opposite isomers are within less than 0·01° in the observed angle of rotation and in the remaining 46 cases the angle lies between 0·01° and 0·02° which is within the limits of experimental error allowed in these measurements.

The Effect of the Solvent on Rotatory Power

The molecular rotatory power, $[M]^{35°}_{5461}$, of the compounds in different solvents is given in Table I. The sequence of decreasing rotatory

Table I

$[M]^{35°}_{5461}$

No.	Structural Formula	Water (80)*	Methyl alcohol (31·2)*	Pyridine (12·4)*	Chloroform (5·2)*
1[c]	 (325)[a]	90·50 (17·28)[b]	90·54 (18·62)[b]	103·6 (20·32)[b]	115·8 (22·82)[b]
	 (355)[a]	94·17 (18·36)[b]	115·6 (22·12)[b]	119·5 (22·35)[b]	124·0 (23·98)[b]
3	 (355)[a]	99·54 (18·61)[b]	115·8 (22·22)[b]	108·6 (20·61)[b]	119·5 (23·29)[b]
4	 (355)[a]	107·4 (20·31)[b]	118·3 (22·47)[b]	116·6 (22·67)[b]	124·28 (24·12)[b]
5	 (341)[a]	66·77 (11·05)[b]	105·2 (20·43)[b]	117·3 (24·60)[b]	118·3 (22·74)[b]
6	 (341)[a]	88·74 (16·35)[b]	97·45 (18·66)[b]	116·6 (23·14)[b]	229·7 (45·27)[b]

*This indicates the Dielectric Constant of the solvent.

(*a*) The values in brackets refer to molecular weights.

(*b*) The values in brackets refer to Kos, the absolute rotation constants.

(*c*) Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.*, 1945, **22**, 267.

powers of the salts of camphor-β-sulphonic acid in different solvents is given below:

(*a*) *o-anisidinocamphor-β-sulphonates* :—

chloroform > pyridine > methyl alcohol > water.

The sequence agrees exactly with that of the dielectric constants in the reverse order.

(*b*) *m-anisidinocamphor-β-sulphonates* :—

chloroform > pyridine > methyl alcohol > water.

The sequence is again exactly in the reverse order of the dielectric constants.

(*c*) *p-anisidino-camphor-β-sulphonates* :—

chloroform > methyl alcohol > pyridine > water.

The sequence is again in the reverse order except for methyl alcohol and pyridine in whose cases the sequence is reversed.

(*d*) *o-aminophenol-camphor-β-sulphonates* :—

chloroform > methyl alcohol > pyridine > water.

The sequence is again in the reverse order of dielectric constants of the solvents except for methyl alcohol and pyridine in whose cases the sequence is reversed.

(*e*) *p-aminophenolcamphor-β-sulphonates* :—

chloroform > pyridine > methyl alcohol > water.

The sequences here is strictly in the reverse order of the dielectric constants.

These sequences for the mercury green line (5461) also hold good for other wavelengths.

Nature of the Racemic Modification

The melting points of all the racemic forms are higher than those of their corresponding optical isomers which shows that they are true *dl*-compounds. However, the nature of the racemic form was further confirmed by adding a small amount of the *d*-form to the corresponding racemic form and in each case it was found that the melting point was lowered. This clearly shows that the racemic camphor-β-sulphonates are true *dl*-compounds.

The Molecular Rotatory Power of Camphor-β-Sulphonic Acid Salts in Aqueous Solution and Comparison of the Values of $[M]_\lambda^{35°}$ of Camphor-β-Sulphonate Ion in Water

Table II gives the values of $[M]_\lambda^{35°}$ for λ varying from 4358 Å.U. to 6708 Å.U. for the different camphor-β-sulphonates in aqueous solution.

TABLE II

$[\alpha]_{\lambda}^{35°}$ In aqueous solution

No.	Camphor-β-sulphonates	Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 4603	Hg 4358
1	*o*-anisidine ..	50·67	56·10	65·16	71·50	76·02	90·48	102·6	113·1	139·4	153·0	162·9	206·3
2	*m*-anisidine ..	52·59	59·73	67·85	72·13	79·64	94·12	108·6	117·7	..	157·5	167·4	..
3	*p*-anisidine ..	54·30	60·63	70·56	77·82	83·26	95·06	114·9	143·0	153·8	170·1	182·8	231·6
4	*p*-aminophenol ..	59·67	66·49	75·72	85·25	90·36	107·4	124·4	136·4	167·0	184·15	197·75	250·6
5	*o*-aminophenol ..	47·85	53·07	61·77	68·74	73·08	88·74	100·9	109·6	139·7	151·4	161·8	208·0

If the salts are completely ionised in dilute aqueous solution, their molecular rotation will be practically the same for a given wavelength, the rotation being independent of the inactive basic ion. In concentrated solution the observed molecular rotation may be greater or less than the value in dilute solution, because it is due both to the active ion and the non-ionised molecule. The results given in Table II show the molecular rotatory power, $[M]_D^{35°}$ of salts of *o*-anisidine as 71·4°, *m*-anisidine 72·13°, *p*-anisidine 77·82°, *o*-aminophenol 68·74° and *p*-aminophenol 85·0°. The molecular rotatory power of camphor-β-sulphonic acid ion in water being 53–54° at 35°, the abovementioned values of molecular rotations of camphor-β-sulphonates of these bases (Table II) indicate that the undissociated salts have higher rotatory power than the completely dissociated molecule and that, therefore, these salts are not completely ionised even in one per cent. aqueous solution.

THE EFFECT OF SUBSTITUENT GROUPS ON ROTATORY POWER

The substituent groups arrange themselves in the following polar series deduced from their inductive capacities:

$$\overset{-}{O}CH_3, OH, Cl, Br, I, CH_3, \overset{+}{H}, COOH, CHO, COCH_3, CN, \overset{+}{N}O_2.$$

(*a*) *Ortho-Substitution.*—On comparing the values of $[M]_{5461}^{35°}$ in water it is found that CH_3, COOH, Cl, OH, I and OCH_3 cause an increase in the rotatory power in the following order:

$$OH > I > COOH > OCH_3 > Cl > CH_3 > H.$$

Thus all the groups except COOH behave in the same sense in conformity with the above mentioned polar series.

TABLE III

No.	Camphor-β-sulphonate of	Water	Methyl alcohol	Ethyl alcohol	Pyridine
1	aniline[a] ..	66·60 (3·400)	105·3 (6·284)	118·63 (6·987)	116·5 (7·570)
2	*o*-toluidine ..	67·35 (3·367)	100·4 (5·865)	117·7 (6·880)	122·7 (7·930)
3	*o*-choloroaniline ..	68·30 (3·078)	86·06 (4·251)	104·7 (5·058)	117·0 (7·125)
4	*o*-iodoaniline ..	84·36 (3·110)	128·76 (5·697)	133·2 (5·058)	144·3 (5·379)
5	*o*-aminobenzoic acid ..	75·44 (3·560)	112·2 (5·950)	118·6 (6·270)	117·0 (7·123)
6	*o*-nitroaniline ..	..	110·8 (3·973)	109·1 (3·666)	115·4 (4·051)
7	*o*-aminophenol ..	85·25 (5·900)	93·77 (6·600)	..	92·07 (6·660)
8	*o*-anisidine ..	71·50 (4·774)	86·32 (5·144)	..	82·50 (5·610)
9	*m*-toluidine ..	66·73 (3·310)	98·31 (5·661)	115·6 (6·790)	120·7 (7·740)
10	*m*-chloroaniline ..	71·70 (3·646)	114·8 (6·386)	122·4 (6·945)	124·2 (6·541)
11	*m*-iodoaniline ..	88·8 (3·268)	124·32 (5·661)	151·4 (6·790)	157·62 (7·740)
12	*m*-aminobenzoic acid ..	71·75 (3·555)	106·7 (5·697)	110·4 (5·618)	128·6 (5·935)
13	*m*-nitroaniline ..	..	127·0 (5·882)	131·0 (5·433)	133·3 (5·185)
14	*m*-anisidine ..	72·13 (5·970)	89·63 (6·340)	..	92·30 (6·170)
15	*p*-toluidine ..	68·50 (3·390)	103·50 (5·950)	120·7 (6·950)	127·5 (7·810)
16	*p*-chloroaniline ..	68·40 (3·510)	103·7 (6·276)	120·7 (6·689)	129·6 (6·420)
17	*p*-iodoaniline ..	76·58 (3·207)	130·98 (5·357)	147·85 (6·310)	156·40 (7·077)
18	*p*-nitroaniline ..	..	112·8 (4·536)	113·6 (4·195)	115·6 (4·782)
19	*p*-aminobenzoic acid ..	67·60 (3·475)	96·86 (5·113)	114·08	131·36 (7·139)
20	*p*-aminophenol ..	68·74 (4·706)	98·79 (5·364)	..	119·88 (6·650)
21	*p*-anisidine ..	77·82 (5·139)	91·43 (6·139)		84·31 (5·694)

(*a*) Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15.
(*b*) Singh, B. K., and Perti, O. N., *Proc. Acad. Sci.*, 1945, **22**, 265.
(*c*) Singh, B. K., and Manhas, K. M. S., *Ibid.*, 1949, **29**, 107.
(*d*) Singh, B. K., and Perti, O. N., *Ibid.*, 1945, **22**, 84.
(*e*) Singh, B. K., and Manhas, K. M. S., *Ibid.*, 1948, **27**, 1.

TABLE IV. *Orthoanisidinocamphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\frac{4\cdot774}{\lambda^2-0\cdot1061}$ 0·3250		$\frac{5\cdot144}{\lambda^2-0\cdot1100}$ 0·3317		$\frac{5\cdot614}{\lambda^2-0\cdot1099}$ 0·3316		$\frac{6\cdot304}{\lambda^2-0\cdot1001}$ 0·3164	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	14·00	14·00	15·00	15·00	16·00	16·00	18·00	18·00
Cd_{6438} ..	15·00	15·50	16·75	16·75	18·00	18·50	20·00	20·00
Li_{6104} ..	18·00	18·00	19·50	19·00	21·50	21·50	23·00	23·00
Na_{5893} ..	19·75	19·75	21·50	21·50	23·50	23·50	25·25	25·25
Hg_{5780} ..	21·00	21·00	23·00	23·00	25·00	25·00	27·00	27·00
Hg_{5461} ..	25·00	25·00	27·00	27·25	30·00	29·75	32·00	31·75
Ag_{5209} ..	29·00	29·00	31·75	32·00	34·75	34·75	36·75	37·00
Cd_{5085} ..	31·00	31·00	34·25	34·25	38·00	38·00	39·75	39·75
Cd_{4800} ..	38·50	38·00	42·50	42·50	46·50	46·50	48·50	48·50
Cd_{4678} ..	42·25	42·75	47·00	47·00	51·50	51·75	53·00	53·00
Li_{4603} .	45·00	45·00	50·50	50·50	57·00	57·00	56·50	56·50
Hg_{4358} ..	57·00	57·00	64·00	64·00	70·50	70·50	70·50	70·00

TABLE V. *Meta-anisidinocamphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases} [\alpha] \\ \lambda_0 \end{cases}$	$\frac{5\cdot072}{\lambda^2-0\cdot1019}$ 0·3192		$\frac{7\cdot324}{\lambda^2-0\cdot0625}$ 0·2761		$\frac{6\cdot173}{\lambda^2-0\cdot1099}$ 0·3316		$\frac{6\cdot625}{\lambda^2-0\cdot1036}$ 0·3218	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	14·50	14·50	19·50	19·50	18·25	18·25	19·50	19·50
Cd_{6438} ..	16·25	16·25	21·25	21·25	20·25	20·25	21·75	21·00
Li_{6104} ..	18·75	18·75	25·00	24·50	23·50	23·50	23·50	23·75
Na_{5893} ..	20·75	20·75	27·00	27·00	26·00	26·00	27·00	27·00
Hg_{5780} ..	22·00	21·75	28·50	28·50	27·50	27·50	29·50	29·50
Hg_{5461} ..	26·00	25·75	33·00	33·00	33·00	32·75	34·25	34·25
Ag_{5209} ..	30·00	30·00	38·00	38·00	38·25	38·25	39·50	39·50
Cd_{5086} ..	32·50	32·50	40·00	40·50	41·50	42·00	42·50	42·50
Cd_{4800} ..	38·50	39·00	47·00	47·00	51·50	51·50	invisible	
Cd_{4678} ..	43·25	43·50	52·00	52·00	56·50	57·00	57·00	57·50
Li_{4603} ..	46·25	46·25	54·00	54·00	60·50	60·75	61·00	61·00
Hg_{4358} ..	invisible		64·50	64·50	78·50	77·50	77·00	77·50

TABLE VI. *Para-anisidinocamphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $[\alpha]_{\lambda_0}$	$\frac{5\cdot139}{\lambda^2-0\cdot1102}$ 0·3320		$\frac{7\cdot660}{\lambda^2-0\cdot0587}$ 0·2423		$\frac{5\cdot694}{\lambda^2-0\cdot1073}$ 0·3276		$\frac{6\cdot434}{\lambda^2-0\cdot1021}$ 0·3196	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	15·00	15·50	19·50	19·50	16·50	16·00	18·50	18·50
Cd_{6438} ..	17·00	17·50	21·50	21·50	18·50	18·50	20·50	20·00
Li_{6104} ..	19·50	19·00	24·50	25·00	21·50	22·00	26·25	26·25
Na_{5893} ..	21·50	21·00	25·50	25·00	23·75	23·75	26·25	26·25
Hg_{5780} ..	23·00	23·00	28·00	28·50	25·00	24·00	27·25	27·25
Hg_{5461} ..	27·50	28·00	32·00	32·00	30·00	30·50	32·50	32·00
Ag_{5209} ..	32·75	33·00	36·00	36·00	34·75	34·75	38·00	38·00
Cd_{5086} ..	35·50	35·00	38·25	38·25	37·50	37·00	40·50	40·50
Cd_{4800} ..	42·50	42·00	44·00	43·00	46·25	46·25	50·00	49·50
Cd_{4678} ..	47·00	48·00	48·00	49·00	48·75	48·75	53·00	53·50
Li_{4603} ..	50·50	50·00	50·00	50·00	54·50	54·50	58·00	57·50
Hg_{4358} ..	64·00	63·00	58·50	59·00	69·00	69·50	73·50	73·50

TABLE VII. *Ortho-aminophenol-camphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $[\alpha]$	$\frac{4\cdot706}{\lambda^2-0\cdot1125}$		$\frac{5\cdot364}{\lambda^2-0\cdot1055}$		$\frac{6\cdot650}{\lambda^2-0\cdot1015}$		$\frac{13\cdot01}{\lambda^2-0\cdot0989}$	
Calculated λ_0	0·3354		0·3248		0·3186		0·3145	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	13·75	13·75	15·50	15·50	21·00	21·00	37·50	37·50
Cd_{6438} ..	15·25	15·25	17·50	17·50	23·50	23·50	41·50	42·00
Li_{6104} ..	17·75	17·75	20·25	20·25	24·50	24·50	48·00	48·00
Na_{5893} ..	19·75	19·75	22·25	22·25	27·00	27·00	53·00	53·00
Hg_{5780} ..	21·00	21·00	23·50	23·50	28·50	28·50	56·00	56·00
Hg_{5461} ..	25·50	25·50	28·00	28·00	33·50	33·50	66·00	66·00
Ag_{5209} ..	29·00	29·00	32·25	32·25	39·50	39·50	76·50	76·50
Cd_{5086} ..	31·50	31·50	35·00	35·00	42·25	42·00	82·50	82·50
Cd_{4800} ..	49·50	49·50	43·00	43·00	50·00	50·00	100·0	100·0
C_{4678} ..	43·50	43·50	47·50	47·50	56·50	56·50	109·5	109·5
Ld_{4603} ..	46·50	46·50	50·50	50·50	62·00	62·00	116·5	116·5
Hg_{4358} ..	59·75	59·75	63·50	63·50	75·00	75·00	145·0	145·0

TABLE VIII. *Para-aminophenol-camphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases} [\alpha] \\ \lambda_0 \end{cases}$	$\frac{5\cdot958}{\lambda^2 - \cdot1089}$ 0·3300		$\frac{6\cdot592}{\lambda^2 - 0\cdot1075}$ 0·3279		$\frac{6\cdot650}{\lambda^2 - 0\cdot1015}$ 0·3186		$\frac{7\cdot071}{\lambda^2 - 0\cdot1114}$ 0·3338	
Line	*d*-	*l*-	*d*-	*l*	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	17·50	17·00	19·25	20·00	19·00	19·00	21·00	21·00
Cd_{6438} ..	19·50	19·50	20·50	20·50	21·50	21·50	23·50	23·50
Li_{6104} ..	22·50	22·50	26·00	26·00	24·50	24·50	27·00	27·00
Na_{5893} ..	25·00	25·00	27·50	27·50	27·00	27·00	30·00	30·00
Hg_{5780} ..	26·50	26·50	29·00	29·00	28·75	28·50	31·75	32·00
Hg_{5461} ..	31·50	31·50	34·00	34·00	33·50	33·50	36·00	36·00
Ag_{5209} ..	36·50	36·50	40·25	40·00	39·50	39·50	44·00	44·00
Cd_{5086} ..	40·00	40·00	43·50	43·00	42·25	42·25	48·00	48·00
Cd_{4800} ..	49·00	49·00	53·50	53·50	52·00	52·00	59·50	59·50
Cd_{4678} ..	54·00	54·00	59·25	59·00	56·50	56·50	65·50	65·50
Li_{4603} ..	58·00	58·50	63·00	63·00	62·00	62·00	70·50	70·50
Hg_{4358} ..	73·50	73·50	80·00	80·00	75·00	75·00	90·00	90·00

In methyl alcohol it is found that the substituent groups CH_3, Cl, OH, and OCH_3 cause a decrease in the value, while I, NO_2 and COOH cause an increase. The order is $I > COOH > NO_2 > H > CH_3 > OH > OCH_3 > Cl$. This agrees with the above mentioned polar series in the reverse sense with minor variations. In ethyl alcohol the groups CH_3, Cl, COOH and NO_2 cause a decrease in the value, while I causes an increase. The order is thus as follows:

$$I > H > COOH > CH_3 > NO_2 > Cl.$$

This does not agree with the above mentioned polar series.

On comparing the values of $[M]_D^{35°}$ in pyridine, however, it is found that the order of decreasing rotatory power is $I > CH_3 > Cl > COOH > H > NO_2 > OH > OCH_3$. This also does not agree with the above polar series.

(*b*) *Meta-substitution.*—On comparing the values in water the order of decreasing rotatory power is $I > OCH_3 > Cl > COOH > CH_3 > H$.

The order agrees with the above mentioned polar series in the same sense except for COOH and I.

In methyl alcohol the order is

$$NO_2 > I > Cl > COOH > H > CH_3 > OCH_3.$$

The order does not agree with the above mentioned polar series.

In ethyl alcohol the order is

$$I > NO_2 > Cl > H > CH_3 > COOH.$$

This again does not agree with the above mentioned polar series.

In pyridine the order is $I > NO_2 > COOH > Cl > CH_3 > H > OCH_3$.

The order does not at all agree with the above mentioned polar series.

(*c*) *Para-substitution :—*

The order in water is

$$OCH_3 > I > OH > CH_3 > Cl > H > COOH,$$

and agrees in the same sense with the above polar series with minor variations.

In methyl alcohol the order is

$$I > NO_2 > H > CH_3 > Cl > OH > COOH > OCH_3.$$

This sequence agrees in the reverse sense with the above mentioned polar series with minor discrepancies.

In pyridine the order is

$$I > COOH > Cl > CH_3 > OH > H > NO_2 > OCH_3.$$

The groups I, Cl, CH_3, OH and COOH cause an increase in the rotatory power and the groups NO_2 and OCH_3 cause a decrease in rotatory power. This is in conformity with the above mentioned polar series except in the case of COOH and OCH_3 groups.

The Effect of Position Isomerism on Rotatory Power

In Table IX the order of rotatory power, $[\alpha]_D^{35°}$, of isomeric anisidinocamphor-β-sulphonates is given:

TABLE IX

Solvent	$[\alpha]_D^{35°}$
Water ..	$p > m > un > o$ ($p > m > un > o$)
Methyl alcohol ..	$p > m > un > o$ ($p > m > un > o$)
Pyridine ..	$m > un > o > p$ ($un < m < p < o$)
Chloroform ..	$p < m < un < o$ ($p < m < un < o$)

The order of kos is also given in brackets. On comparing the values of $[\alpha]_D^{35°}$, the sequence of position isomerides in all solvents is $p > m > un > o$ with the exception of pyridine, in which case the order is $m > un > p > o$. Similar results are obtained when comparison is made for the values of kos. These sequences agree with both Frankland's[3] "lever arm" hypothesis and its electrostatic modification as suggested by Rule,[4] except in the case of pyridine.

In Table X are recorded the decreasing order of the specific rotatory powers, $[\alpha]_D^{35°}$, of the position isomers of aminophenolcamphor-β-sulpho-

TABLE X

Solvent	$[\alpha]_D^{35°}$
Water ..	$p > un > o$ ($p > un > o$)
Methyl alcohol ..	$p > un > o$ ($p > un > o$)
Pyridine ..	$un > p > o$ ($un > p > o$)
Chloroform ..	$p > un > o$ ($p > un > o$)

nates in different solvents. The decreasing order of the rotation constants, kos, are also given in brackets.

Here also we find that the sequence is in agreement with Frankland's[3] "lever arm" hypothesis and its electrical modification as suggested by Rule,[4] except in the case of pyridine.

Experimental

Camphor-β-sulphonates (d-, l-, and dl-) of o-, m- and p-anisidine and o- and p-aminophenol.—Molecular proportions of the amines and the acids were separately dissolved in ethyl acetate and on mixing the two solutions, the salts crystallised out. They were repeatedly recrystallised from absolute ethyl alcohol as fine white needles. They are very soluble in pyridine and water, less so in methyl alcohol, chloroform and ethyl alcohol and insoluble in acetone and benzene.

Anisidinocamphor-β-Sulphonates

Ortho-salts:

d-form, m.p. 153° C.; S, 9·2%.

l-form, m.p. 153° C.; S, 9·2%.

dl-form, m.p. 171° C.; S, 9·2%.

Meta-salts:

d-form, m.p. 103° C.; S, 8·0%.

l-form, m.p. 103° C.; S, 8·9%.

dl-form, m.p. 161° C.; S, 8·9%.

Para-salts:

d-form, m.p. 159° C.; S, 8·8%.

l-form, m.p. 159° C.; S, 8·8%.

dl-form, m.p. 170° C. S, 9·2%.

$C_{17}H_{25}O_6NS$ requires S, 9·0%.

Aminophenolcamphor-β-Sulphonates

Ortho-salts:

d-form, m.p. 165° C.; S, 9·5%.

l-form, m.p. 165° C.; S, 9·0%.

dl-form, m.p. 170° C.; S. 9·1%.

Para-salts:

d-salt, m.p. 151° C.; S, 9·12%.

l-salt, m.p. 151° C.; S, 9·45%.

dl-salt, m.p. 172° C.; S, 9·2%.

$C_{16}H_{23}O_6NS$ requires S, 9·35%.

Summary

1. The rotatory dispersion of stereoisomeric salts of *o*-, *m*- and *p*-anisidine and *o*- and *p*-amino-phenols with camphor-β-sulphonic acid (*d*- and *l*-) is found in different solvents to obey Drude's one-term equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$; it is, therefore, " Simple ".

2. The *d*- and *l*-forms of these compounds possess identical rotatory power and thus support Pasteur's Law of Molecular Dissymmetry.

3. The sequence of rotatory power in different solvents is in the reverse order of their dielectric constants with minor variations.

4. The racemic forms of the salts are found to be true *dl*- compounds.

5. The influence of hydroxy and methoxy groups on the rotatory power is discussed.

6. The effect of position isomerism on rotatory power has also been discussed.

Acknowledgement

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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part VI. Magnetic Susceptibility Measurements. The Systems: KNO_3-Pb $(NO_3)_2$-H_2O. & NH_4NO_3-$Pb(NO_3)_2$-H_2O

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This paper is intended to emphasize the importance of magnetic susceptibility studies in the investigation of complex formation in solution. We have already given a brief account of our work.[1] Fuller details are now presented.

A modified Decker Balance[2] specially designed and constructed for this type of work by Dr. K. N. Mathur was placed at our disposal. The main features of this instrument are that a test body, *viz.*, a small glass rod ½ inch long, is rigidly attached in the middle, to a thin long rod whose other end is fixed to a quartz fibre mounted to a torsion head. The readings are taken in somewhat the same manner as with Curie Wilson Balance.[3] The test piece hangs horizontally inside a glass tube with inlet and outlet for introducing and withdrawing liquids, fixed in position between the poles of the electromagnet. The most important improvement is that the glass container has another jacket in which water circulates from a thermostat, there being an arrangement for thermometric observations at the inlet and outlet of the jacket.

The importance of maintaining the temperature constant has not been appreciated by some workers, who seem to think that because one is measuring diamagnetic susceptibilty which is independent of temperature, there is no need to keep the temperature constant. The fact is that the equation for the calculation of susceptibility contains terms which are very much dependent upon temperature, *viz.*, the susceptibility of air and the density of liquid; and unless the temperature is kept constant calculated values of diamagnetic susceptibility are bound to be discordant.

A current of two amperes in the electromagnet gave the required field strength which was kept constant during each observation. The solution needed for the experiment was 25 c.c. The formula used to evaluate the susceptibility was:—

$$\chi_{soln}\,\rho_{soln} = \chi_{\omega}\cdot\rho_{\omega} + (\chi_{\omega}\,\rho_{\omega} - \chi_{a}\,\rho_{a})\,\frac{\theta_{\omega} - \theta_{soln}}{\theta_{a} - \theta_{\omega}}$$

(where χ is the susceptibility, ρ density, θ the deflection, the subscripts ω, a, denote water and air).

The working of the apparatus was checked by making determinations of the susceptibility of liquids of known values, taking water as reference substance with $\chi = -0{\cdot}72 \times 10^{-6}$.

The following values were obtained for benzene and acetic acid:—

	Expt.	*I.C.T*
Benzene	$-0{\cdot}711 \times 10^{-6}$	$-0{\cdot}712 \times 10^{-6}$
Acetic acid	$-0{\cdot}522 \times 10^{-6}$	$-0{\cdot}521 \times 10^{-6}$

Solutions.—Stock solutions of lead nitrate and potassium nitrate of 1·0 M strength were prepared. 20 c.c. KNO_3 were pipetted out into a measuring flask of capacity 60 c.c. the requisite quantity of lead nitrate added from a standard burette, and the solution made up to the mark (60 c.c.), by addition of water. In this way 25 solutions were made in which the concentration of alkali nitrate remained the same, namely $\frac{1}{3}$ M, while that of lead nitrate varied systematically from 0·0 M to $\frac{2}{3}$ M.

Observations.—To secure adequate precision in measurement a number of determinations on standard substances were carried out. The glass rod and the container were carefully cleaned with chromic acid, distilled water, conductivity water and finally alcohol, and then allowed to dry before use. The readings for air and water were repeated before and after the observations recorded with each set of solutions. A mean of three readings was taken for calculation. The values of χ_{sol} were then plotted against the concentration of lead nitrate, *i.e.*, against the number of c.c. of $Pb(ON_3)_2$ added to 20 cc. KNO_3.

The results obtained are recorded in the following table, and are represented graphically in Fig. 1.

Temperature = 35 ± 0·1° C.

θ_{air} = 71° 1′ 0″ θ_{water} = − 6° 12′ 40″

c.c. $Pb(NO_3)_2$ added to 20 c.c. KNO_3	$\chi_{sol} \times 10^{-6}$	c.c. $Pb(NO_3)_2$ added to 20 c.c. KNO_3	$\chi_{sol} \times 10^{-6}$
0	−0·7068	18	−0·6400
2	−0·6997	20	−0·6300
3	−0·6917	22	−0·6261
4	−0·6874	24	−0·6194
5	−0·6823	26	−0·6130
6	−0·6803	28	−0·6073
7	−0·6783	30	−0·6024
8	−0·6723	32	−0·5968
9	−0·6693	34	−0·5910
10	−0·6640	36	−0·5850
12	−0·6582	38	−0·5800
14	−0·6523	40	−0·4740
16	−0·6474		

SYSTEM

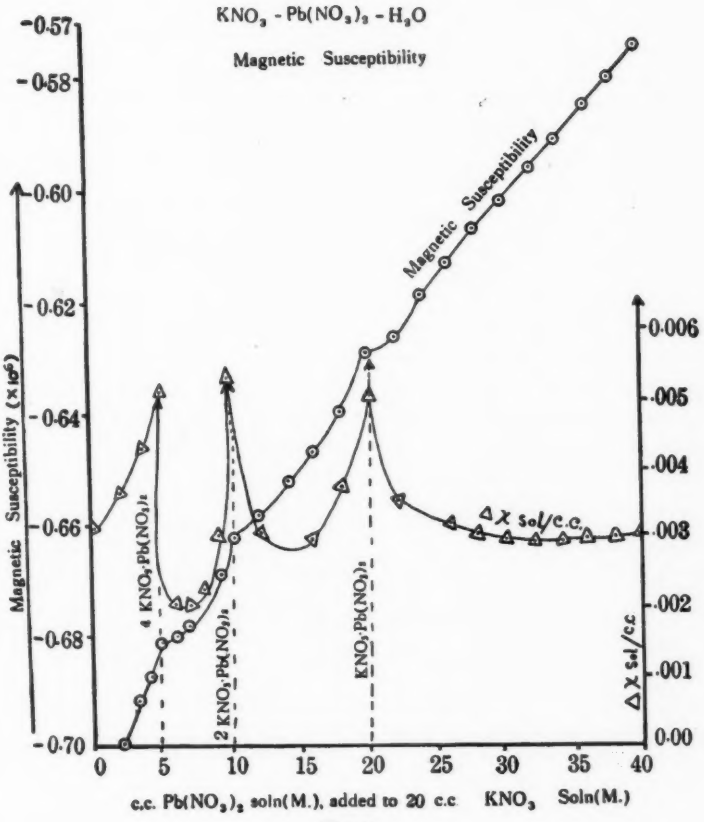

FIG. 1

The curve (Fig 1.), indicates 3 breaks at 5, 10, 20 c.c. of Pb $(NO_3)_2$. When plottings are made with " the change of χ_{mol}/c.c.", the periodicity of the curve is brought out more prominently. The ratios of concentrations of the two salts follow stoicheiometric laws at the points of inflexion corresponding to the compounds:—

4 $KNO_3 \cdot Pb\ (NO_3)_2$ and 2 $KNO_3 \cdot Pb\ (NO_3)_2$ and $KNO_3 \cdot Pb\ (NO_3)_2$

Similar experiments were carried out with the system: NH_4NO_3-Pb $(NO_3)_2$-H_2O, and analogous results obtained.* Here also the evidence for the formation of three compounds is unequivocal: *viz.*,

4 $NH_4NO_3 \cdot Pb(NO_3)_2$, 2 $NH_4NO_3 \cdot Pb(NO_3)_2$ and $NH_4NO_3 \cdot Pb(NO_3)_2$

These investigations show that magnetic susceptibility can, like other physico-chemical properties (viscosity, rheochor, parachor, conductivity, freezing point and E.M.F.) be employed in the investigation of complex formation in solution.

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* Values omitted for economy of space.

FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part VII. The System : $LiNO_3$-Pb $(NO_3)_2$-H_2O

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In previous communications[1] it has been shown that three definite complexes are produced in solution in each of the systems: KNO_3-Pb $(NO_3)_2$-H_2O and NH_4NO_3-Pb $(NO_3)_2$-H_2O, while no such formation can be detected in the system: $NaNO_3$-Pb $(NO_3)_2$-H_2O. It was of interest to extend the investigation to other alkali nitrates. This paper reports the results obtained with the system: $LiNO_3$-Pb $(NO^3)_2$-H_2O. The properties investigated were viscosity, conductivity and transport number.* An examination of the literature reveals that no work has been done on this system.

Experimental

Lithium nitrate (B.D.H., A.R.) was recrystallised thrice with conductivity water, and its purity confirmed by converting a known amout of lithium nitrate into sulphate. Stock molar solutions of lithium nitrate and lead nitrate were prepared. A small flask was calibrated to hold 30 c.c. solution. 10 c.c. of lithium nitrate (1 M.) were pipetted into the flask to which the requisite volume of lead nitrate (1 M.) was added from a standard burette and the mixture made up to the mark (30 c.c.) by addition of water. In this way 25 solutions were made in which the concentration of lithium nitrate was kept constant (*viz.*, $\frac{1}{3}$ M.), while that of lead nitrate varied systematically from 0·0 M to $\frac{2}{3}$ M.

The solutions were of the following composition

SOLUTION NUMBER ..	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
c.c. $Pb(NO_3)_2$ added to 10 c.c. $LiNO_3$ solution	0	1	1·5	2	2·5	3	3·5	4	4·5	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

* pH measurements have also been carried out, which are described in Part VIII of this series.

Viscosity and Conductivity

The methods for determination of these physico-chemical properties were the same as employed in the previous parts of this series. (For economy of space tabulated results have been omitted.) When the values of both viscosity and conductivity were plotted against the concentration of lead nitrate, smooth curves were obtained (Fig. 1). All the plots were regular indicating no tendency for the formation of complex compounds in these systems. Both these properties (one being a bulk property, while the other, ionic property) lead to the same conclusion. The results are also similar to those obtained with $NaNO_3$.

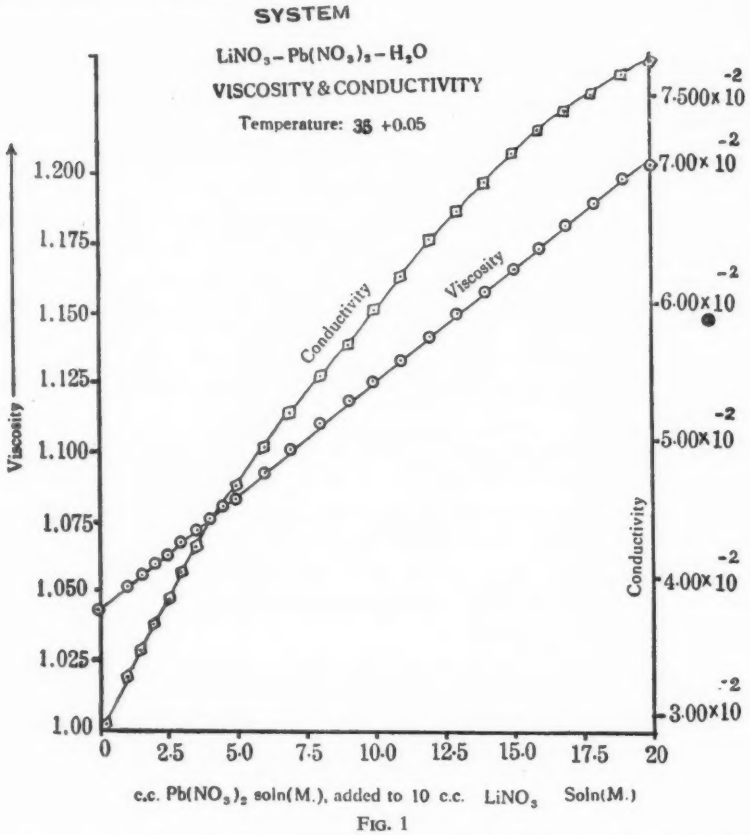

Fig. 1

In order to have a quantitatively comparable idea of the behaviour of $LiNO_3$ and $NaNO_3$, experiments on transport number of Pb ion were carried out.

Transport Number

Transport number of Pb ion was determined in M/20 lead nitrate solution. The method adopted was the same as described in Part V of this series. Three determinations were made with $Pb(NO_3)_2$ solution and the experiments repeated with mixtures containing the molecular ratios:

$LiNO_3$: $Pb(NO_3)_2$ 1 : 1, 2 : 1 and 4 : 1.

In these solutions the concentration of lead nitrate was kept constant (*viz.* M/20), while that of $LiNO_3$ varied.

The results are tabulated in Tables I, II and III.

Table I

Transport number of Pb ion in M/20 lead nitrate solution

Expt. No.	Concn.	Wt. of solution (anodic compt.)	Wt. of $Pb(NO_3)_2$ after (electrolysis)	Wt. of H_2O (calc.)	Wt. of $Pb(NO_3)_2$ before (electrolysis)	Total current equivalent to :		$Pb(NO_3)_2$ (migrated)	Transport number
						Cu	$Pb(NO_3)_2$		
I	M/20	27·4852	0·4612	27·0240	0·4237	0·0138	0·0719	0·0344	0·4785
II	M/20	28·5118	0·4922	28·0196	0·4392	0·0196	0·1021	0·0491	0·4809
III	M/20	27·5131	0·4741	27·039	0·4240	0·0184	0·09587	0·04571	0·4774

Mean Value = 0·4789

Table II

Transport number of Pb ion. The system: $LiNO_3$-$Pb(NO_3)_2$-H_2O

Soln. No.	Concentration	Wt. of soln. (anode)	Wt. of $Pb(NO_3)_2$ after (electrolysis)	Wt. H_2O (calc.)	Wt. of $Pb(NO_3)_2$ before (electrolysis)	Total current equivalent to :		$Pb(NO_3)_2$ migrated	Transport number	Mean value
						Cu	$Pb(NO_3)_2$			
I	M/20 $Pb(NO_3)_2$ + M/20 $LiNO_3$	28·9487	0·5390	28·4097	0·4807	0·0210	0·1094	0·05112	0·4672	0·4666
		28·0044	0·5277	27·4767	0·4647	0·0226	0·1177	0·05470	0·4648	
II	M/20 $Pb(NO_3)_2$ + M/10 $LiNO_3$	28·7406	0·5552	28·1854	0·4747	0·0284	0·1480	0·0675	0·4560	0·4547
		28·8058	0·5299	28·2759	0·4761	0·0190	0·0990	0·0452	0·4534	
III	M/20 $Pb(NO_3)_2$ + M/5 $LiNO_3$	28·5608	0·4884	28·0724	0·4372	0·0178	0·09274	0·04154	0·4477	0·4460
		29·1356	0·5225	23·6131	0·4611	0·0212	0·1104	0·04906	0·4443	

TABLE III

Percentage change in transport number of lead ion in the presence of different alkali nitrates

Mol. Ratio RNO_3: $Pb(NO_3)_2$	$LiNO_3$	$NaNO_3$*	KNO_3*	NH_4NO_3*
1 : 1	2·69%	6·4%	38·18%	35·3%
2 : 1	5·05%	14·32%	60·20%	57·2%
4 : 1	6·87%	18·60%	72·2%	68·7%

* Values reproduced from Part V, of this series.

Table III records the percentage change effected in the transport number of Pb ion in the presence of different alkali nitrates. It is obvious that the precentage change in transport number of Pb ion in the presence of $LiNO_3$ is of a very low order as compared with those in the case of KNO_3 and NH_4NO_3 systems. It is even less than that observed in the case of the $NaNO_3$ system. In the case of KNO_3 and NH_4NO_3 systems the precentage change varies from 35% to 72%, while even in $NaNO_3$ system the maximum percentage is 18%. But in $LiNO_3$ system the maximum percentage change is only 7%. This means that the tendency for the formation of complex compounds in the $LiNO_3$ system is even less than that in the case of $NaNO_3$ as is to be expected from the position of lithium in the Periodic Table.

CONCLUSION AND SUMMARY

Viscosity, conductivity and transport number measurements with $LiNO_3$-$Pb(NO_3)_2$-H_2O system indicate that in lithium nitrate the tendency for the formation of complex compounds is even less than in $NaNO_3$ systems. The latter showed some evidence of complex formation but no stoicheiometric relationship was observed. KNO_3 and NH_4NO_3 on the other hand gave definite evidence of the formation of three complexes in each case. Complex formation seems to be conditioned by the position of the alkali element in the Periodic Table. Confirmation of this view has been sought by an investigation of systems containing rubidium nitrate, the results of which will be reported in due course.

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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part VIII. pH Measurements

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In the preceding parts of this series[1] I—VII. (*Proc. Ind. Acad. Sci.*, A, 1948, **27**, 284-99, 343-60 and subsequent issues), it has been shown that among the alkali nitrates, Li and Na salts exhibit little tendency for the formation of complex compounds with lead nitrate, while K,NH_4 and Rb nitrates form three complexes of the general formulæ:

4 $RNO_3 \cdot Pb(NO_3)_2$; 2 $RNO_3 \cdot Pb(NO_3)_2$; and $RNO_3 \cdot Pb\ (NO_3)_2$

(where R stands for K,NH_4 or Rb). We now report results based on measurements of pH change. This measurement has not perhaps been fully exploited in connection with the investigation of complex formation, though Britton has indicated the importance of pH change in the study of complex cyanides ("Hydrogen Ions", 1942, p. 158). See also Ghosh and co-workers[2] (*J.I.C.S.* 1945, **22**, 287-300).

In the present problem, the constituent salts are lead nitrate and alkali nitrate, of which the first one, being derived from a weak base and strong acid can be expected to hydrolyse in aqueous solution and give a low pH value which may show a steady variation with change in concentration. The alkali nitrate on the other hand, may not show any such variation since the concentration remains constant.

If we assume the existence of a compound such as $K_4\ [Pb\ (NO_3)_6]$, derived from the hypothetical acid $H_4\ [Pb\ (NO_3)_6]$, the latter may reasonably be regarded as a weak acid compared with nitric acid. An alkali salt derived from it must therefore on hydrolysis give a pH value on the alkaline side of the scale.

Thus the formation or otherwise of the complex compounds must reflect itself on the pH of the solutions. Looking at the problem from another point of view, the formation of the complex according to the equation:

$$4\ KNO_3 + Pb(NO_3)_2 \rightleftarrows K_4[Pb(NO_3)_6]$$

virtually amounts to the removal of lead nitrate and hence a diminution in concentration of the salt. This must also reflect itself on the pH of the solution.

Thus a measurement of the pH of the various solutions must yield interesting information about the formation of the complexes.

Experimental

Molar solutions of lead nitrate, potassium nitrate, ammonium nitrate and lithium nitrate were prepared. [The salts taken were extra pure

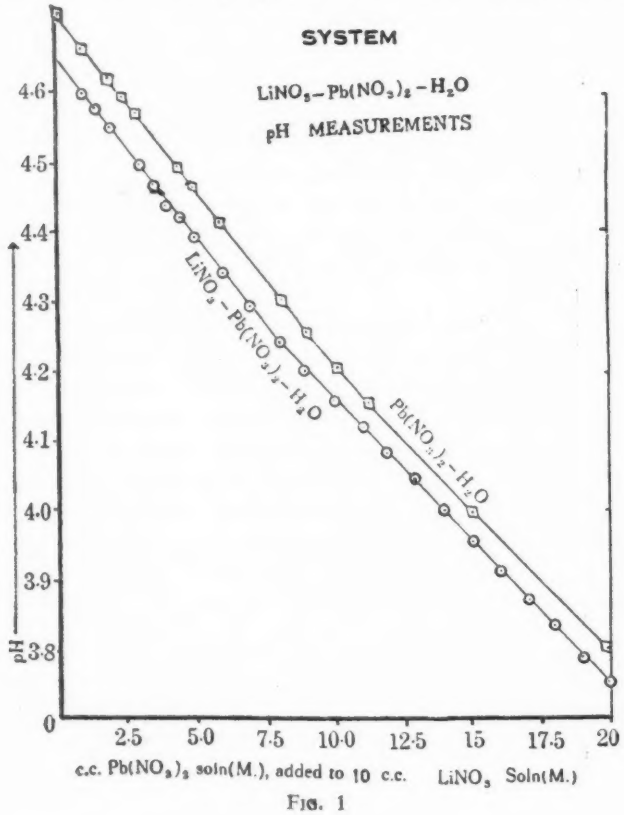

Fig. 1

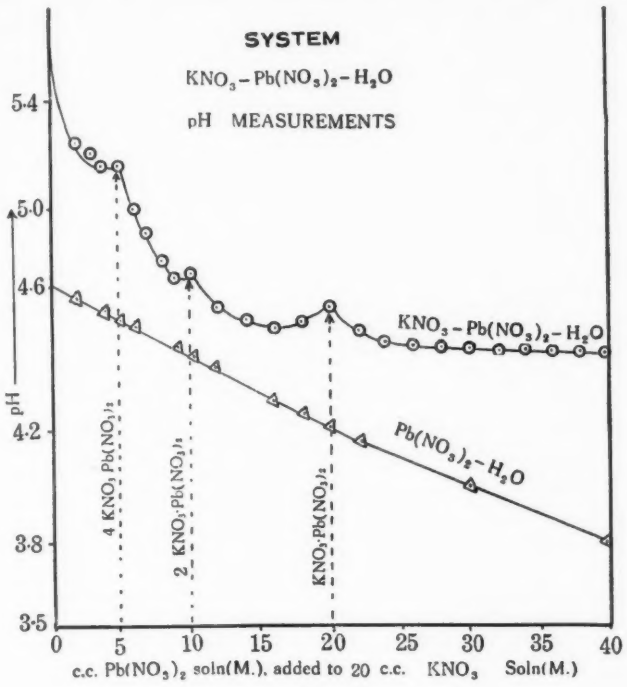

FIG. 2

(B.D.H., A.R) and were recrystallised thrice with conductivity water]. These solutions were stored in pyrex bottles that had been previously steamed. Sets of 25 solutions were prepared in the study of each system. The method employed for the preparation of these solutions was the same as described in the previous parts of this series.

The solutions were of the following composition:—

Solution Number ..	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
c.c. $Pb(NO_3)_2$ (1·0 M) added to 20 c.c. alk. nitrate (1·0 M)	0	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40

For comparative purposes, a set of solutions containing only lead nitrate was also prepared.

For pH measurements the glass electrode assembly already described by Nayar and Srivastava[3] was used. The potentiometer (L. N. " Student " pattern) was calibrated by standard methods.

Buffer solutions were prepared having pH values between 2–9 and the corresponding E.M.F.s measured. A standard graph (a straight line) was thus obtained connecting pH with E.M.F. and employed in measuring the pH of the nitrate solutions. The standard graph was periodically checked.

The results obtained with the various solutions are recorded in the following table and are represented graphically in Figs. 1, 2 and 3, where the pH values are plotted against the volume in c.c. of lead nitrate, added to a fixed quantity of alkali nitrate (20 c.c.).

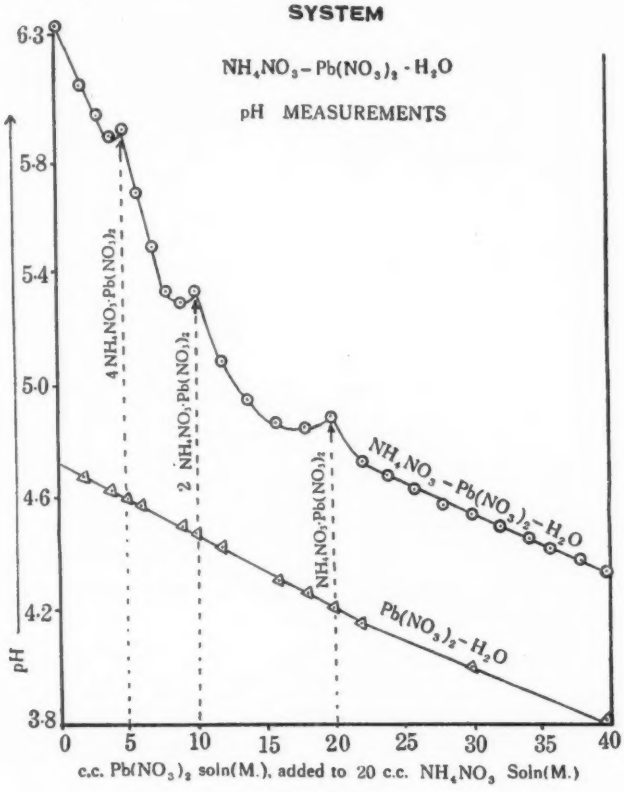

FIG. 3

Observations.—It will be noticed that the plots are regular in the case of $Pb(NO_3)_2$-H_2O, as also in the system: $LiNO_3$-$Pb(NO_3)_2$-H_2O, while there are three kinks in each of the systems containing KNO_3 and NH_4NO_3. These occur exactly at the points corresponding to the formation of the three compounds. (*a*) $4\,RNO_3 \cdot Pb(NO_3)_2$, (*b*) $2\,RNO_3 \cdot Pb(NO_3)_2$ (*c*) $RNO_3 \cdot$

OBSERVATIONS

TABLE I

Soln. No.	c.c. $Pb(NO_3)_2$ added to 20 c.c. alk. nitrate	pH $Pb(NO_3)_2-H_2O$ system	pH $LiNO_3$ system (*a*)	pH KNO_3 system (*b*)	pH NH_4NO_3 system (*c*)
1	0	..	6·70	6·98	6·28
2	2	4·67	4·60	5·24	6·08
3	3	..	4·58	5·20	5·98
4	4	4·625	4·55	5·15	5·90
5	5	4·60	4·52	5·15	5·92
6	6	4·58	4·50	5·00	5·70
7	7	..	4·47	4·92	5·50
8	8	..	4·44	4·81	5·35
9	9	4·50	4·32	4·75	5·30
10	10	4·47	4·39	4·76	5·33
11	12	4·42	4·34	4·65	5·10
12	14	..	4·29	4·60	4·96
13	16	4·30	4·24	4·57	4·88
14	18	4·25	4·20	4·59	4·85
15	20	4·20	4·16	4·65	4·89
16	22	4·15	4·12	4·55	4·73
17	24	..	4·08	4·52	4·68
18	26	..	4·04	4·51	4·63
19	28	..	4·00	4·50	4·58
20	30	4·00	3·91	4·50	4·54
21	32	..	3·87	4·50	4·50
22	34	..	3·83	4·49	4·45
23	36	..	3·78	4·49	4·41
24	38	..	3·75	4·49	4·36
25	40	3·80	3·72	4·49	4·32

(*a*) means the system : $LiNO_3$–Pb $(NO_3)_2$–H_2O.
(*b*) means the system : KNO_3–Pb $(NO_3)_2$–H_2O.
(*c*) means the system : NH_4NO_3–Pb $(NO_3)_2$–H_2O.

Pb $(NO_3)_2$ (where R stands for K or NH_4) and confirm the conclusions arrived at on the basis of other physico-chemical measurements.

A close study of the various graphs gives instructive information on the mechanism of the complex formation. The following points may be noted:—

(1) *Change in pH of Lead nitrate solution.*—A linear relationship between acidity and concentration of lead nitrate is noticed (Graph I). The pH value changes from 4·67 for $\frac{M}{30}$ molar solution to 3·8 for solution of $\frac{M}{5}$ M strength.

(2) *$LiNO_3$-Pb $(NO_3)_2$-H_2O.*—The graph is parallel to and below that of the previous one, there being a uniform difference of about 0·05 pH units. Excepting for a slight tendency to make the solution more acidic $LiNO_3$ has no marked effect on Pb $(NO_3)_2$. Additive law of mixtures is strictly obeyed.

(3) *KNO_3 (or NH_4NO_3)-Pb $(NO_3)_2$-H_2O.*—while the addition of $LiNO_3$ tends still further to lower the pH value of Pb $(NO_3)_2$ solution, both KNO_3

and NH_4NO_3 raise the pH so much so that both the graphs of the two systems are above that of $Pb(NO_3)_2$. The final pH values for solutions containing 40 c.c. of $Pb(NO_3)_2$ are also instructive.

	No alkali nitrate	$LiNO_3$	KNO_3	NH_4NO_3
pH	3·80	3·72	4·49	4·32

(*a*) The nitrates of potassium and ammonium seem to check the hydrolysis of lead nitrate. This cannot be due to the increasing concentration of the nitrate ion, since lithium nitrate does not show this effect. Resistance to the hydrolysis of lead nitrate must therfore be a specific property of the nitrates of potassium and ammonium. The shape of the two curves contrasted to that of lithium nitrate shows that the additive law is not obeyed.

(*b*) An increase in pH can only mean a virtual disappearance of lead nitrate from the field of action. If we now assume complex formation, *e.g.*,

$$4\,KNO_3 + Pb(NO_3)_2 \rightleftharpoons K_4\,[Pb(NO_3)_6]$$

the observed difference can be easily explained. The complex hydrolyses to a smaller extent than lead nitrate and the pH is therefore higher.

(*c*) A 100% formation of $K_4\,[Pb(NO_3)_6]$ is improbable, since we cannot crystallise it out. The compound apparently exists only in solution and in equilibrium with its constituent nitrates. On removal of the solvent there is reversal of the equilibrium and the constituents separate out.

(*d*) The constant value of pH in the case of the potassium nitrate system beyond a certain concentration of lead nitrate, is due to buffer-effect in which the complex: $K\,[Pb(NO_3)_3]$ participates.

Conclusion and Summary

pH measurements indicate that there is no complex formation in the system: $LiNO_3$-$Pb(NO_3)_2$-H_2O, while three definite complexes are present in solution in the systems: KNO_3-$Pb(NO_3)_2$-H_2O and NH_4NO_3-$Pb(NO_3)_2$-H_2O. The molecular formulæ of these compounds are the same as indicated in the previous parts of this series. The pH measurements fully confirm the results obtained by the study of other physico-chemical properties of the systems.

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A NEW SYNTHESIS OF ASARONIC ACID AND ALDEHYDE AND THEIR DERIVATIVES

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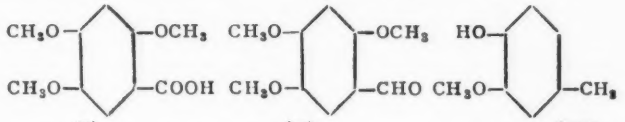
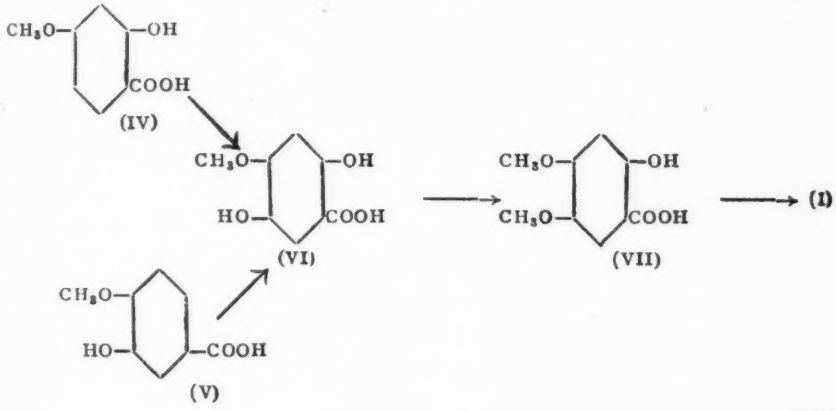
Samples of asaronic acid (I) and aldehyde (II) were required in connection with the identification of certain degradation products of naturally occurring compounds in this laboratory. Apart from the oxidation of asarylic aldehyde and asarone[1, 7, 8] asaronic acid was also made in the past[2] starting from creosol (III) and following a number of steps.



The preparation becomes considerably simplified by employing Elbs persulphate method[3] of oxidation. Either 4-O-methyl resorcylic acid (IV) or isovanillic acid (V) could be used for this purpose, the product being 2: 5-dihydroxy-4-methoxy benzoic acid (VI). This could be methylated in stages yielding 4 : 5-dimethoxy-2-hydroxy benzoic acid (VII) and finally asaronic acid (I). The samples thus prepared agree in every respect with the description in the literature of asaronic acid. The dimethoxy-salicylic acid (VII) is an important degradation product of dehydro-deguelin[4] and

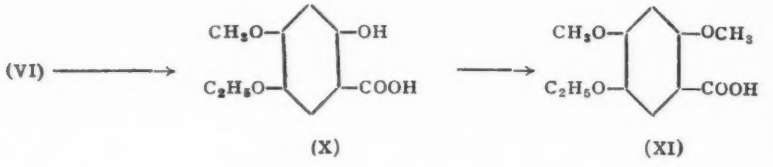


was originally synthesised by Head and Robertson[5] starting from veratrol. The present synthesis constitutes considerable simplification.

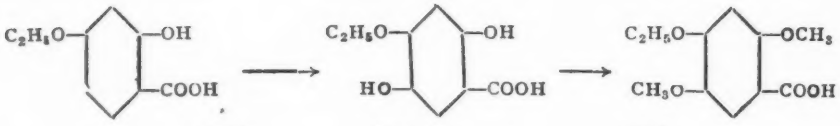
For the above purposes β-resorcylic acid (VIII) itself can be directly employed. It undergoes oxidation but the yield of the oxidation product, *i.e.*, 2: 4: 5-trihydroxy benzoic acid (IX)[6] is rather poor. It can be methylated to asaronic acid (I).

(VIII) (IX)

Further the new method is convenient for preparing the mixed (ethyl methyl) ethers of hydroxyquinol carboxylic acid that have been used by Head and Robertson[7] in connection with the constitution of aesculin. By the partial ethylation of 2: 5-dihydroxy-4-methoxy benzoic acid (VI) and subsequent methylation 2: 4-dimethoxy-5-ethoxy benzoic acid (XI) is obtained. Its isomer, 2: 5-dimethoxy-4-ethoxy benzoic acid (XII) can be prepared from the 4-ethyl ether of β-resorcylic acid (XIII)[10] by subjecting it to oxidation with potassium persulphate and finally methylating it fully.

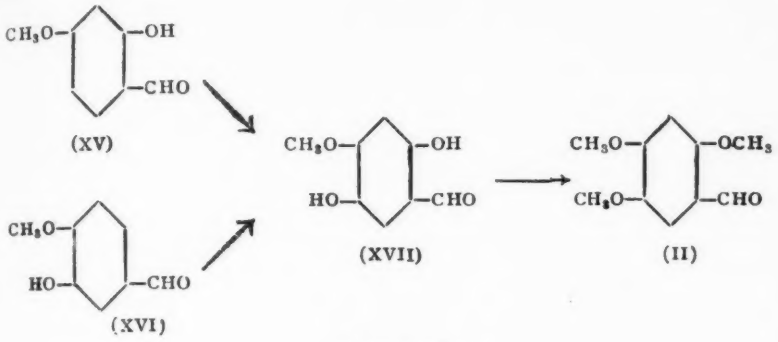


(X) (XI)



(XIII) (XIV) (XII)

Similar procedures can be adopted also for the preparation of asarylic aldehyde[1] (II) starting from resorcylic aldehyde monomethyl ether (XV) or from isovanillin (XVI). Good yields are obtained in their oxidation with persulphate producing 2: 5-dihydroxy-4-methoxy benzaldehyde (XVII) which can be methylated to yield asarylic aldehyde (II). This trimethoxy benzaldehyde was prepared earlier from the ethers of hydroxyquinol by employing the Gattermann reaction.[7, 8]



EXPERIMENTAL

2: 5-*Dihydroxy*-4-*methoxy benzoic acid* (*VI*)

(i) 2-Hydroxy-4-methoxy-benzoic acid was conveniently prepared by methylating resorcylic acid (24 g., 1 mole) with dimethyl sulphate (17 c.c., 1·1 mole) and excess of aqueous alkali (80 c.c. of 20%).

To a solution of 2-hydroxy-4-methoxy benzoic acid (10·0 g.) in aqueous sodium hydroxide (8·0 g. in 90 c.c.) cooled to 10°, was added dropwise an aqueous solution of potassium persulphate (17·0 g. in 300 c.c.) with stirring, in the course of 4 hours. After allowing to stand for 24 hours at room temperature the solution was neutralised with dilute hydrochloric acid and extracted with ether repeatedly to remove the unreacted compound. To the remaining aqueous solution was added concentrated hydrochloric acid (60 c.c.) and sodium sulphite (8·0 g.) and the mixture kept in a water-bath at 80° for 30 minutes. The solution was cooled and extracted with ether. On distilling off ether from the extract a brown solid was left. This crystallised from aqueous alcohol as colourless rectangular rods melting at 201° (decomp.). Yield, 3·5 g. With alcoholic ferric chloride it gave a blue colour which changed to green and finally faded. (Found: C, 47·2; H, 5·0; Loss on drying at 110° in vacuo 8·8%, $C_8H_8O_5$, H_2O requires C, 47·5; H, 5·0 and loss 8·9%.)

(ii) Isovanillic acid[9] (4·0 g.) was subjected to oxidation with aqueous potassium persulphate (8·0 g. in 160 c.c.) in alkaline medium (6·0 g. of sodium hydroxide in 40 c.c. of water). On working up the reaction product as in the above experiment the quinol carboxylic acid was obtained as a brown amorphous solid. After repeated crystallisations from aqueous alcohol it came out as colourless rectangular rods and prisms melting at 201° (decomp.). Yield, 1·4 g. A mixed melting point with the sample obtained above was undepressed.

2-Hydroxy-4: 5-dimethoxy benzoic acid (VII)

The above dihydroxy compound (VI) (0·8 g.) in dry benzene (30 c.c.) was refluxed with dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (4·0 g.) for 6 hours. The potassium salts were filtered off and washed with hot benzene. On distilling off the solvent from the filtrate a colourless solid was obtained. When crystallised from water it yielded the methyl ester of 2-hydroxy-4: 5-dimethoxy benzoic acid as long prismatic needles melting at 95°. This ester (0·6 g.) was hydrolysed by heating with 5% aqueous alkali (20 c.c.) for half an hour on a boiling water-bath. The product obtained on acidification was crystallised from aqueous alcohol. 2-Hydroxy-4: 5-dimethoxy benzoic acid separated out as rhombohedral prisms melting at 210-11° (decomp.).[4, 5] A mixed melting point with 2: 5-dihydroxy-4-methoxy benzoic acid was considerably depressed. It gave a violet blue colour with alcoholic ferric chloride. Yield, 0·4 g.

2: 4: 5-Trimethoxy benzoic acid (Asaronic acid) (I)

2: 5-Dihydroxy-4-methoxy benzoic acid (VI) (0·5 g.) in acetone (30 c.c.) was treated with freshly distilled dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (6·0 g.) and the mixture refluxed for 12 hours. The potassium salts were filtered and washed with warm acetone. On removing acetone from the filtrate and adding water to the residue a brown amorphous solid was obtained. This was filtered and hydrolysed by heating with 5% aqueous alkali on a boiling water-bath for half an hour. The resulting product when crystallised from benzene-petroleum ether yielded asaronic acid as colourless needles melting at 143°.[1, 2] It gave no colour with alcoholic ferric chloride. Yield, 0·4 g.

2: 4: 5-Trihydroxy benzoic acid (IX)

An ice-cold solution of β-resorcylic acid (VIII) (15·0 g.) in aqueous sodium hydroxide (12·0 g. in 100 c.c.) was treated with aqueous potassium persulphate (30·0 g. in 400 c.c.). After 24 hours the solution was worked up as usual. The product was a brown solid (3·0 g.) and was difficult to purify; after a number of crystallisations from water it yielded hydroxy quinol carboxylic acid as fine needles melting at 217-18° (decomp.).[6] Mixed melting point with β-resorcylic acid was depressed. The trihydroxy acid gave a violet blue colour with alcoholic ferric chloride. Yield, 1·0 g. When this acid (0·6 g.) in acetone (50 c.c.) was methylated with dimethyl sulphate (1·3 c.c.) and potassium carbonate (10·0 g.) and the resulting ester was hydrolysed with 5% alkali it yielded asaronic acid.

2-Hydroxy-4-methoxy-5-ethoxy benzoic acid (*X*)

2: 5-Dihydroxy-4-methoxy benzoic acid (VI) (1·0 g.) in acetone (80 c.c.) was treated with freshly distilled diethyl sulphate (1·3 c.c.) and anhydrous potassium carbonate (6·0 g.) and refluxed for 12 hours. The potassium salts were filtered and acetone distilled off from the filtrate. The sticky solid thus obtained was hydrolysed by heating with 5% aqueous sodium hydroxide (40 c.c.) for half an hour. The solution on acidification yielded the monohydroxy acid as an amorphous solid. It crystallised from aqueous alcohol as rectangular rods melting at 194° (decomp.). It gave a stable violet blue colour with alcoholic ferric chloride. Yield, 0·6 g. (Found: C, 56·2; H, 6·0; $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%.)

2: 4-*Dimethoxy-5-ethoxy benzoic acid* (*XI*)

The preceeding compound (X) (0·1 g.) in acetone (30 c.c.) was methylated with dimethyl sulphate (0·4 c.c.) and anhydrous potassium carbonate (2·0 g.) by refluxing for 24 hours. The resulting product was hydrolysed with 5% aqueous sodium hydroxide (10 c.c.). 2: 4-Dimethoxy-5-ethoxy benzoic acid crystallised from water as rectangular rods melting at 137°.[7] It gave no colour with alcoholic ferric chloride.

2: 5-*Dihydroxy-4-ethoxy benzoic acid* (*XIV*)

To an ice-cold solution of 2-hydroxy-4-ethoxy benzoic acid[10] (XIII) (3·0 g.) in aqueous sodium hydroxide (1·3 g. in 15 c.c.) was added dropwise potassium persulphate (3·5 g. in 70 c.c. of water) during 4 hours. The reaction product was worked up as usual. The dihydroxy acid crystallised from aqueous alcohol as thin rectangular rods, melting at 202-4° (decomp.). With alcoholic ferric chloride it gave a violet blue colour which slowly changed to green and finally faded. Yield, 0·5 g. (Found: C, 54·2; H, 5·3; $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%.)

2: 5-*Dimethoxy-4-ethoxy benzoic acid* (*XII*)

The above dihydroxy acid (XIV) (1·0 g.) in acetone (100 c.c.) was methylated with dimethyl sulphate (1·8 c.c.) and anhydrous potassium carbonate (5·0 g.) by refluxing for 20 hours. The dimethyl ether crystallised from aqueous alcohol as rectangular rods melting at 130-31°.[7] It did not give any colour with alcoholic ferric chloride. Yield, 0· 6 g.

2: 5-*Dihydroxy-4-methoxy benzaldehyde* (*XVII*)

(i) 2-Hydroxy-4-methoxy benzaldehyde was made earlier by Ott and Nauen[11] by the methylation of resorcylic aldehyde with dimethyl sulphate and alcoholic potash. It is now found that the preparation is more conveniently carried out in boiling dry benzene solution (5 hours) with 1·1 mole of dimethyl sulphate and excess of anhydrous potassium carbonate.

2-Hydroxy-4-methoxy benzaldehyde (XV) (5·0 g.) was dissolved in pyridine (5 c.c.) and aqueous sodium hydroxide (4·0 g. in 50 c.c.) and the solution cooled in ice. A solution of potassium persulphate (10·0 g. in 250 c.c. of water) was added dropwise in the course of 4 hours. After 24 hours the product was worked up as usual. It crystallised from alcohol as colourles rectangular plates and prisms melting at 209° (decomp.).[7] Yield, 1·0 g. With alcoholic ferric chloride it gave a bluish green colour which slowly faded.

(ii) Isovanillin (4·0 g.) in aqueous sodium hydroxide (3·2 g. in 40 c.c.) was treated with potassium persulphate (8·0 g. in 200 c.c.) under conditions identical with those employed above. 2: 5-Dihydroxy-4-methoxy benzaldehyde crystallised from alcohol and melted at 209° (decomp.).[7] A mixed melting point with the sample obtained in the previous experiment was not depressed. Yield, 1·6 g.

2: 4: 5-*Trimethoxy-benzaldehyde* (*Asarylaldehyde*) (*II*)

The dihydroxy aldehyde (XVII) (0·5 g.) in acetone (40 c.c.) was refluxed for 10 hours with dimethyl sulphate (1·0 c.c.) and potassium carbonate (6·0 g). The reaction product when crystallised from water yielded asaryl-aldehyde as rectangular rods melting at 114°.[7, 8] It did not give any colour with alcoholic ferric chloride.

Summary

Asaronic acid is conveniently prepared from 4-O-methyl-β-resorcylic acid and isovanillic acid by oxidation with alkaline persulphate and subsequent methylation. Useful partial methyl ethers and mixed methyl-ethyl ethers are also made by adopting this method. Similarly asarylic aldehyde is obtained from 4-O-methyl-β-resorcylic aldehyde and isovanillin.

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A NOTE ON THE COMPONENTS OF THE BARK OF *PRUNUS PUDDUM*

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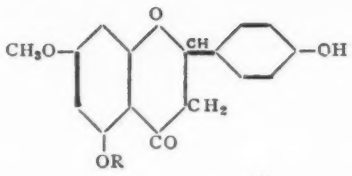
In connection with our work on the synthesis of sakuranetin[1] we needed some quantity of the natural sample for purposes of comparison. It was prepared by the extraction of the bark of *Prunus puddum* which had been earlier shown to contain it.[2] In the course of their examination of this bark Chakravarti, *et al.* recorded the presence of puddumetin which was later shown to be the same as genkwanin,[3] sakuranetin, and also an isoflavone which they named prunusetin.[4] In our experiments described in this paper using a modified method of extraction improved yields of these substances have been obtained. Sakuranetin (I *a*) occurs in the largest amount (1% of the air-dried bark) along with small quantities of its glucoside sakuranin (I *b*).[5] Genkwanin (II) and prunusetin are obtained in yields of 0·2% and 0·6% respectively. In their study of sakuranetin obtained from this source Chakravarti and co-workers[2] recorded that they could not get the colourless diacetate melting at 98°. This derivative was originally prepared by Asahina and co-workers[6] and also by Zemplen,[7] *et al.* and inability to obtain it would throw some doubt about the identity of the natural flavanone. We have therefore examined this reaction and are able to record that the particular diacetate melting at 98° could be prepared from this sample of sakuranetin obtained from *Prunus puddum* bark thus confirming the identification. Further this sample of sakuranetin could also be dehydrogenated by means of iodine yielding genkwanin (II). Earlier Chakravarti, *et al.*[2] reported that they could not carry out this transformation using selenium dioxide. The reaction using iodine is of a general nature and has been recently studied in detail with a number of examples.[8] Its application in the present case establishes elegantly the interrelationship between these two components obtained from the same bark (I *a* and II).

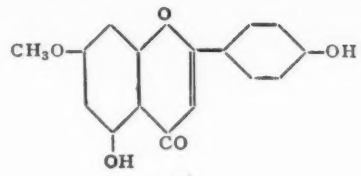
A careful examination of prunusetin has now shown that it is a slightly impure sample of prunetin (III). Chakravarti and Bhar[4] considered that it was different from prunetin and that it was a new substance because of the somewhat lower melting points they obtained for it and for its acetate and because of their failure to carry out partial methylation yielding the



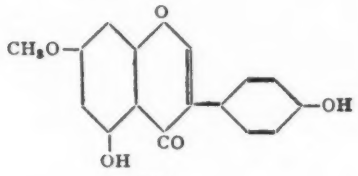
(I)

(*a*) R = H

(*b*) R = Glucose residue



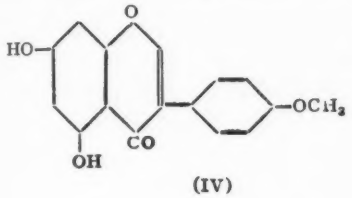
(II)



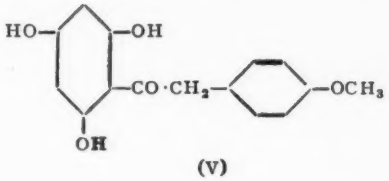
(III)

monomethyl ether. They could only get the dimethyl ether which was identical with genistein trimethyl ether. Of the three monomethyl ethers of genistein, prunetin is the 7-methyl ether earliest to be discovered in nature.[9] More recently the 4′-monomethyl ether (IV) has been obtained both synthetically[10] through the ketone (V) and from a natural source also as biochanin.[11] Chakravarti and Bhar came to the conclusion that prunusetin was the rather unusual 5-monomethyl ether of genistein; it would thus differ from the other two components of the *Prunus puddum* bark which are 7-methyl ethers. Their conclusion seemed to be erroneous even when their own observations were considered. For example, they recorded that prunusetin gives a brownish violet colour with ferric chloride which would suggest that in this compound the 5-hydroxy group is free; the presence of 7 and 4′-hydroxyls alone does not give rise to this colour. The insolubility of prunusetin in aqueous sodium carbonate would also indicate that the hydroxyl in the 7-position is not free. It is now found that careful purification of prunusetin by means of its acetate raises the melting point to 242° and its properties are identical with those of prunetin. Its partial methylation could be accomplished by using one mole of dimethyl sulphate and excess of anhydrous potassium carbonate in anhydrous acetone medium. The product, a dimethoxy compound, has the same melting point and properties as monomethyl prunetin (VI). Its acetate also has the required melting point. There seems to be no doubt therefore that prunusetin is essentially prunetin though slightly impure and the new name is not necessary. Not only does the bark the *Prunus puddum* contain representatives of the three major groups of anthoxanthins, a

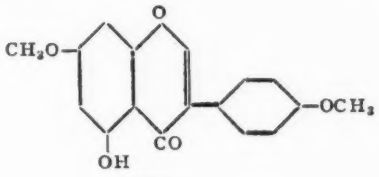
flavanone, flavone and isoflavone, but they all have the common feature that they are 7-methyl ethers of 5:7:4′-trihydroxy compounds.



(IV)



(V)



(VI)

EXPERIMENTAL

Extraction

The sun-dried bark of *Prunus puddum* (2 kg.) was powdered and extracted twice with cold alcohol by percolation. Each extraction was carried out for 48 hours. The deep red alcoholic extract was concentrated by distillation as much as possible and the concentrate (about 300 c.c.) was allowed to stand when after two days a deep red sticky solid separated out. This was filtered and extracted twice with hot benezene (100 c.c.) by refluxing on a water-bath for half an hour. The benzene extract (Fraction A) was set aside and worked up as described later. The residue on the filter was then boiled twice with water (100 c.c.) and filtered. The aqueous solution (Fraction B) contained the glucosidic portion. The solid left behind was then dissolved in excess of hot alcohol (Fraction C).

Fraction A (*Sakuranetin*) (I *a*)

The benzene solution when cooled slowly deposited a colourless crystalline solid which on recrystallisation from acetic acid was obtained as colourless prismatic needles melting at 151-52°. This product agreed in all its properties and colour reactions with sakuranetin. On evaporating the remaining benzene solution a pale yellow solid was obtained. This was recrystallised first from benzene and subsequently from acetic acid whereby a further quantity of sakuranetin was obtained. Total yield 20 g. (1% of the dry bark).

Acetylation

The sample of sakuranetin (0·5 g.) was dissolved in acetic anhydride (5 c.c.) and a few drops of pure concentrated sulphuric acid added. The solution was heated on a water-bath for 10 minutes and left at room temperature for 6 hours. It was then poured into ice-water with stirring. The semisolid that separated was extracted with ether. On evaporating the ether solution the product solidified slowly when kept in a vacuum desiccator. It crystallised from ethyl acetate as colourless tiny prisms melting at 98-99°. It gave no colour with ferric chloride in alcoholic solution.

Oxidation with iodine: Preparation of genkwanin (II)

Sakuranetin (0·5 g.) was dissolved in alcohol (10 c.c.), sodium acetate (1·5 g.) added and the solution boiled. To this a boiling solution of iodine (0·5 g.) in alcohol was added slowly. In the beginning there was rapid decolourisation and the completion of the reaction was indicated by a permanent colouration due to iodine. On cooling the solution a bright yellow solid separated. This was filtered and washed with sulphur dioxide water. It crystallised from alcohol in the form of yellow needles melting at 285-7°. A further quantity of the substance could be obtained by concentrating the alcoholic solution, diluting with water and crystallising the precipitated solid. Yield, 0·35 g. Its alcoholic solution gave a violet colour with ferric chloride and a scarlet red colour with magnesium and hydrochloric acid. It was identical in its properties with genkwanin and the mixed melting point with the natural sample described below was undepressed. (Found: C, 67·2; H, 4·1; $C_{16}H_{12}O_5$ requires C, 67·5; H, 4·2%.)

Fraction B (Sakuranin I b)

Since on cooling the aqueous solution and allowing to stand no product separated it was concentrated under reduced pressure on a water-bath (20 c.c.). The concentrated solution was shaken with excess of ether and allowed to stand. After a few days a colourless crystalline solid had slowly separated out. It crystallised from dilute alcohol as short needles melting at 210-12°. Its alcoholic solution gave a bright red colour with magnesium and hydrochloric acid but gave no colour with ferric chloride. It gave a deep green colour with concentrated nitric acid and dissolved in alkali giving a yellow solution. It agreed in all its properties with the description of sakuranin.[5] The aqueous mother-liquor when hydrolysed with 7% sulphuric acid yielded sakuranetin. Yield of sakuranetin 0·5 g.

Fraction C: Genkwanin and prunetin (II and III)

The alcoholic solution deposited on cooling a yellow crystalline solid which when recrystallised from alcohol melted at 285° and was identical

with genkwanin. The mother-liquor yielded on concentration a brownish yellow solid melting between 228° and 240°. This was boiled with small quantities of alcohol thrice and filtered. The residue yielded some more of pure genkwanin when recrystallised from ethyl acetate. The combined alcoholic extract deposited on cooling pale yellow needles melting at 236-8°. Recrystallisation from ethyl acetate raised the melting point to 238-39°. Yield, genkwanin 2 g., and prunusetin 6 g.

The prunusetin sample was acetylated by boiling with acetic anhydride and fused sodium acetate. The mixture was poured into ice-water, the colourless crystalline acetate was filtered, washed with water and dried. It crystallised from ethyl acetate as colourless rhombohedral prisms melting at 225-26° and agreed with the description of prunetin acetate. (Found: C, 64·9; H, 4·2; $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%.) Deacetylation of the above acetate using alcoholic hydrochloric acid and crystallisation of the product from alcohol gave pure prunetin melting at 240-41°.

Prunetin monomethyl ether

Prunusetin sample (0·5 g.) was dissolved in dry acetone (20 c.c.), dimethyl sulphate (0·15 c.c.) and anhydrous potassium carbonate (1 g.) were added and the mixture refluxed for 6 hours. It was then filtered and the potassium salts washed with hot acetone. On distilling off acetone a pale yellow solid was obtained. It crystallised from ethyl acetate as thin rectangular plates melting at 139-40°. (Genistein dimethy ether, m.p. 140–41°.)[12] It gave a reddish brown colour with violet tinge with ferric chloride in alcoholic solution and it was sparingly soluble in aqueous sodium hydroxide (Found: C, 68·2; H, 5·0; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%.)

Its acetate prepared by using acetic anhydride and sodium acetate crystallised from ethyl acetate as colourless rectangular prisms melting at 202–3°. (Found: C, 66·8; H, 5·0; $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·7%.) Deacetylation of the acetate and crystallisation of the product from ethyl acetate gave prunetin monomethyl ether, m.p. 140-41°.

Prunetin dimethyl ether

Prunusetin sample (0·5 g.) was methylated by boiling with excess of dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1·5 g.) in dry acetone solution (20 c.c.) for 15 hours. Acetone was then distilled off and water added. The solid was filtered and washed with water. It crystallised from dilute alcohol as colourless needles melting at 161-62°; genistein trimethyl ether has m.p. 161-62°.[12] It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution.

SUMMARY

The stem bark of Prunus puddum yields sakuranetin (I *a*), sakuranin (I *b*), genkwanin (II) and prunetin (III). The identification of sakuranetin is confirmed by the preparation of its diacetate and conversion to genkwanin. Prunusetin is shown to be only a slightly impure sample of prunetin. Though the components belong to different groups of anthoxanthins, they have the common feature that they are all 7-methyl ethers of 5: 7: 4′-trihydroxy compounds.

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